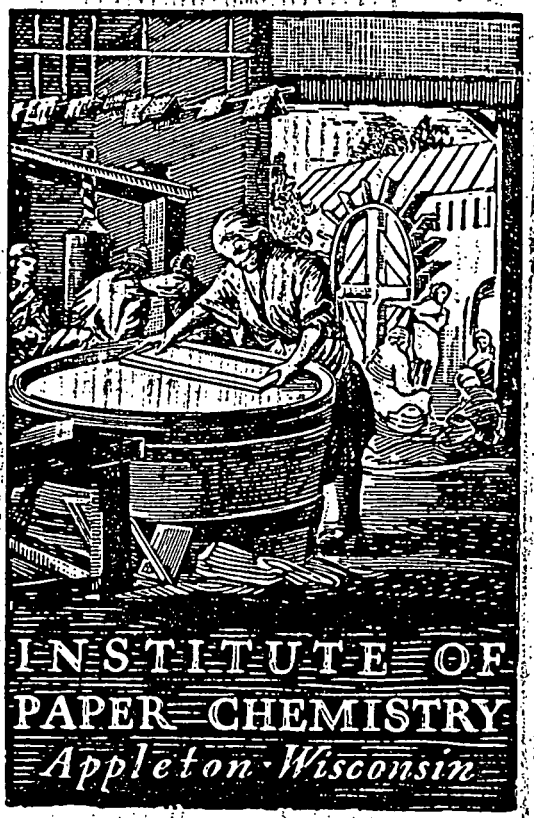

"STUDY OF EVAPORATOR SCALING"
SOLUBLE CARBONATE-SULFATE SCALES

Project 3234

Report Two
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

January 25, 1977

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SUMMARY

Water soluble, sulfate-carbonate scales are one of the two most prevalent types formed during evaporation of alkaline black liquor. These deposits form by precipitation of sodium carbonate and sodium sulfate from a supersaturated solution which arises when the liquor is concentrated beyond the saturation limit. Scale growth is governed by solubility conditions in the bulk liquor rather than by local conditions at the hot surface. It sets in at a critical solids content directly related to solubility limits and can become quite rapid once the critical solids content is exceeded. Most liquors reach saturation at about 50 to 55% solids.

Solubility curves are presented which can be used to estimate the critical solids content of a given liquor. The effect of liquor composition on soluble scale formation is in accordance with the solubility curves. Saturation concentrations are lowered by increases in carbonate and sulfate content, proportion of sulfate, and amounts of other sodium salts. The addition of NaOH to the liquor to maintain a high residual alkali (8.3% on solids or 14 gpl in weak liquor, as Na_2O) did not prevent scale formation.

The effect of evaporator operating variables on carbonate-sulfate scaling is directly related to their effect on local solids content. There was no indication that stable supersaturation could be maintained, without scaling, through a proper choice of operating variables.

The overall heat transfer coefficient was found to be strongly dependent on the fraction of the tube surface needed to supply the sensible heat requirement.

Local coefficients are much lower in the subcooled zone than they are in the net boiling zone. A substantial improvement in overall heat transfer coefficient could be obtained by shortening or eliminating the subcooled zone, provided that this does not adversely affect flow stability.

Carbonate/sulfate scaling in black liquor evaporators can be readily prevented or minimized by means of one or more of the following steps.

1. Reduce the discharge solids content from the evaporator to a level below the saturation solids content of the liquor.
2. Reduce the amount of sulfate and carbonate in the liquor so that the saturation solids content is greater than the discharge solids content.
3. Provide entrained solids to encourage precipitation in the bulk liquor instead of the hot surface.
4. Maintain operation as stable as possible.
5. Install a fiber filter in the weak liquor line.

INTRODUCTION

Deposition of scale in evaporator tubes increases the resistance to heat transfer and can be responsible for a marked decrease in evaporator capacity. A recent survey of evaporator operation in the alkaline pulping industry (described in Progress Report One) (1) showed that average coefficients for black liquor evaporation systems varied from 130 to more than 300 Btu/hr ft^2 °F. The primary reason for this wide range in evaporator performance was evaporator scaling.

Different types of scales can form during evaporation of black liquor. They are often classified according to the degree of difficulty in removing them. The two most prevalent types are soluble scales and calcium scales.

Soluble scales consist mainly of precipitated sodium sulfate and sodium carbonate. These materials are soluble in water or weak black liquor, and the scales can be controlled by boiling out the evaporator with water or by periodically cycling weak liquor through the evaporator.

Calcium scales contain calcium carbonate as the main component. These are not water soluble and must be removed by other means such as acid cleaning, thermal shocking, hydroblasting, etc. Some calcium scales can be removed by boiling out with water, probably because of the thermal shocks involved.

This report is concerned only with soluble carbonate-sulfate scales. Subsequent reports will treat other types of scales.

NATURE OF SOLUBLE SCALES

Confusion exists in the literature as to the nature of soluble scale. The revised edition of Pulp and Paper Manufacture, Vol. 1, (2) states that water-soluble scales are usually Na_2SO_4 caused by excess unreduced sulfate in the black

liquor, which scales out on the hot surface because of the inverted solubility vs. temperature curve for Na_2SO_4. They give a value of 5-6% Na_2SO_4 (on dry solids) as the critical limit. Berry (3) also lists sodium sulfate scale due to the inverted solubility behavior of Na_2SO_4. Letonmyaki, et al. (4) found deposits on the evaporator tube wall to be rich in Na_2SO_4 and Na_2CO_3 as well as ligneous and resinous substances. Dedrichs and Hedstrom (5) pointed out that in black liquors, the double salt, Burkeite, ($2Na_2SO_4 \cdot Na_2CO_3$) is more likely to precipitate than either of the single salts. They found analyses of deposits to agree closely with the composition of the double salt. Stacie and Wilhelmsen (6) mention a precipitated scale — primarily soluble inorganic salts such as Na_2SO_4, Na_2CO_3 and some black liquor solids. Thus, there is universal recognition that sulfate is involved, a lesser awareness of the involvement of carbonate, and some indications that organic materials may also be present.

Solubility limits for certain components in alkaline process black liquors were determined in a previous study at the Institute and the results published (7). This study showed that the materials most likely to precipitate were Na_2CO_3 and Na_2SO_4, forming a solid phase with a composition close to that of Burkeite ($2Na_2SO_4 \cdot Na_2CO_3$). There was little evidence for organic precipitation in concentrating liquors up to 65% solids. Most organic which did precipitate was residual soap. Temperature did not have a major effect on the solubility of liquor components over the range 100-140°C.

These data suggest that soluble scales should be basically a crystalline deposit of Na_2SO_4 and Na_2CO_3, with a composition close to that of $2Na_2SO_4 \cdot Na_2CO_3$, formed by precipitation from a supersaturated solution. Resinous material could be present if it is not removed effectively in a prior soap skimming operation. Ligneous substances would not normally be present unless the residual alkali

level in the liquor was below that needed to stabilize the lignin colloid. Fibers can be readily incorporated into the scale and serve as a reinforcing agent. However, they will not form a scale by themselves.

IDENTIFICATION OF SOLUBLE SCALES

The proper identification of an evaporator scaling problem must be based on an analysis of the composition of the deposits. Thus, soluble scales would be better identified as those deposits which are rich in Na_2SO_4 and Na_2CO_3. Since these scales are by definition water soluble they are quite easy to remove by boiling out the evaporator. Thus, they can be removed without opening up the evaporator, and so few direct samples of the deposit are taken. For this reason soluble scales are often identified indirectly on the basis of their ease of removal by boiling out rather than by direct analysis of their composition. This assumes that all deposits which are removable by boiling out with water are water-soluble scales. This is not necessarily true. Some calcium scales can also be removed by boiling out (probably because of thermal stresses). Since many scales in black liquor evaporators are controllable by boiling out with water and are not clearly identified by analysis of composition, there is a good deal of uncertainty regarding the relative severity of different types of scales and much confusion about methods for minimizing scales.

SIGNIFICANCE OF SOLUBLE SCALES

Soluble scales are an important problem. In the survey presented in Progress Report One (1), 19 of the 46 kraft and soda mills which participated reported a soluble carbonate-sulfate scale. It is not at all clear how reliable this number is nor to what extent the identification of sulfate-carbonate scale is based on direct evidence.

It has commonly been assumed that soluble scales are rapid growing scales which can be removed fairly easily, while calcium (and other) scales form much more slowly and remain behind as a residual scale when the soluble scale is removed by boiling out. This leads to the concept that soluble Na_2CO_3-Na_2SO_4 scales are responsible for the short-term deterioration in evaporator performance which can be recovered by boiling out, while calcium and other insoluble scales cause a gradual degradation in performance level.

The data obtained in the survey did not support this concept. No correlations could be established between boilout frequencies or the extent of capacity loss between cleanings, and expected soluble scale parameters. Instead, correlations of boilout frequencies with the calcium content of the liquor were found. This was interpreted to mean that calcium scales could be at least partly controlled by boiling out with water, and that over the entire industry, calcium scales had a greater effect on evaporator performance (even short-term performance) than soluble scales.

Soluble scales are almost certainly encountered in concentrators. Practically all black liquors become saturated in Na_2CO_3 and Na_2SO_4 at solids contents of 55% or lower. Thus, precipitation of Na_2CO_3 and Na_2SO_4 is always possible when concentrating to 60-65% solids. The occurrence of soluble scales must be provided for in the design of concentrator systems.

It is evident that soluble scales can cause problems in multiple-effect evaporator systems. In general, these appear to have less impact on evaporator performance (loss of capacity and need for cleaning) than do calcium scales. Soluble scales are likely to be encountered in concentrators, and provisions must be made in concentrator designs to allow for them.

CONTROL OF SOLUBLE SCALES

Approaches to the control of soluble scales which have been used or suggested include the following:

1. Reduce the amounts of Na_2SO_4 and Na_2CO_3 in the liquor. This usually takes the form of maintaining high reduction efficiencies in the recovery furnace and a high degree of conversion in the causticizing plant. The emphasis is mainly on Na_2SO_4. A maximum level of 5-6% Na_2SO_4 on the liquor solids is often used as a guideline.

2. Maintain a high residual active alkali in the liquor. This could take the form of caustic or white liquor addition to weak black liquor or the use of excess active alkali during cooking. The solubility study (7) showed that caustic addition will tend to decrease the solubility of Na_2CO_3 and Na_2SO_4 in the black liquor. Thus, any beneficial effect of high residual alkali would seem to be associated with improved lignin stability. A minimum residual active alkali concentration of 6 gpl as Na_2O in weak liquor is often used as a guideline.

3. Effective soap removal. As liquors are concentrated, soaps will precipitate and must be removed. Residual soap will contribute to soluble scale formation.

4. Keep fiber out of liquor. Fiber will reinforce scales as they form and increase the severity of the scaling problem. A filter on the weak liquor can be used for fiber removal. A concentration of 0.25-0.3 lb fiber per 1000 gal of weak liquor is reported to be a good target in avoiding problems in high solids evaporation.

5. Reduce discharge solids level from multiple-effect evaporators. Since solubility limits of Na_2CO_3 and Na_2SO_4 are approached rather rapidly at about 50% solids, soluble scale problems can be avoided by staying safely below the critical solids level. This approach is feasible only if there is sufficient direct contact evaporator (or concentrator) capacity to reach the desired final solids concentration.

6. Eliminate superheated steam to first effect. Several mills have reported a reduction in scaling problems when desuperheaters were installed on the steam supply.

7. Increase velocity of liquor in tubes. This can be accomplished by multipass arrangements or by recirculating concentrated liquor.

8. Eliminate low velocity, sensible-heat zones. Internal preheaters, after heaters, or external forced circulation preheaters can be used to eliminate the stagnant, sensible-heat zone.

The effectiveness of these various procedures is often subject to debate. A definitive knowledge of the factors controlling the growth of soluble scales would permit a rational approach to their control.

OBJECTIVES OF STUDY

The overall objectives of this study were to obtain a better understanding of the process of soluble scale formation and to use this insight to formulate measures for minimizing or eliminating the problem. Specific objectives were as follows:

1. Obtain data on soluble scale formation under well-defined conditions.

a. Analysis of scale composition to verify Na_2SO_4 and Na_2CO_3 as the main components and determine if significant amounts of organic substances take part.

b. Measurements of scaling rate as a function of controlled sets of variables.

2. Evaluate the role of equilibrium solubility limits.

a. Verification of soluble scale formation as a crystallization process.

b. Determine if conditions favor local scaling at the wall when the bulk liquor is unsaturated.

c. Determine if it is possible to operate without scaling when the liquor is supersaturated.

3. Determine the key parameters controlling soluble scale formation.

a. Liquor composition variables.

b. Evaporator operating conditions.

c. Tube surface conditions.

4. Reevaluate measures for controlling soluble scale in the light of the results of the study.

An experimental single-tube evaporator was constructed and used to obtain data on scale formation under controlled conditions. These data, together with information gathered in the survey and data on solubility limits in black liquors obtained in a previous study (Project 3136) were used to meet the objectives of the study.

REVIEW OF SOLUBILITY WORK

Solubility limits for various components in black liquor were determined in an earlier group project (Project 3136). The results of this study were published in a paper "Solubility Limits in Black Liquor" presented at the International Symposium on Recovery of Chemicals and Energy held at the 80th National Meeting of AIChE in Boston, September, 1975 (7). Copies of this paper are available as IPC Technical Paper Series, Number 6. Since this work is very pertinent to the soluble scale problem, a brief review is given below.

Solubility data were obtained under equilibrium conditions (constant temperature and no net interchange between precipitated solids and liquor components in solution). Liquors were equilibrated with precipitated solids in closed, stirred vessels immersed in a temperature-controlled oil bath. Samples of the solution phase were obtained by using fritted glass filters to exclude precipitated solids. Compositions of the solid phase were determined by an adaptation of Schreinemaker's rest method which corrects for entrained solution in the solid phase sample. Liquors from nine different mills were used in the program.

CARBONATE-SULFATE SOLUBILITY

It was established that Na_2CO_3 and Na_2SO_4 are the major components which precipitate on concentrating black liquors up to solids contents as high as 65%. The solubility behavior of Na_2CO_3 and Na_2SO_4 in black liquor is very similar to their behavior in the Na_2CO_3-Na_2SO_4-NaOH-H_2O system. Over most of the range of liquor composition, the precipitated phase is a solid solution of Na_2CO_3 and Na_2SO_4 ranging in composition from (1.4 to 2.2)$Na_2SO_4 \cdot Na_2CO_3$ (65-75% Na_2SO_4 by weight). Temperature has very little effect on the solubility over the range 100-140°C.

A general correlation for the solubility limits of Na_2CO_3 and Na_2SO_4 in black liquor was developed. The main parameters involved are the total amount of Na_2CO_3 and Na_2SO_4 present, the carbonate-sulfate ratio, the solids content of the liquor, and the effective sodium. The latter is all of the sodium in the liquor other than that accounted for by the carbonate and the sulfate, and may be defined as

$$\text{Effective sodium} = \text{total sodium} - 23\left[\frac{Na_2CO_3}{53} + \frac{Na_2SO_4}{71}\right]$$

Saturation curves for a Na_2CO_3/Na_2SO_4 ratio of 80/20 are given in Fig. 1. This figure can be used to determine the solids content at which a given liquor becomes saturated or conversely the amount of Na_2CO_3 and Na_2SO_4 which can be held in solution at a given liquor solids content. A correction factor to extend Fig. 1 to other Na_2CO_3/Na_2SO_4 ratios is given in Fig. 2. The value of soluble Na_2CO_3 + Na_2SO_4 read from Fig. 1 is to be multiplied by the correction factor.

The relations expressed in Fig. 1 and 2 were able to correlate Na_2CO_3-Na_2SO_4 solubilities for nine different liquors over a solids range from 40-65% and a temperature range of 100-140°C with a mean deviation of -0.6% and a standard deviation of 7.4%. This general solubility correlation is only approximate. There are definite differences, usually minor, associated with the different composition of different liquors.

The correlation in Fig. 1 shows that the solubility of Na_2CO_3 and Na_2SO_4 is decreased as the effective sodium content of the liquor is increased. Thus, the addition of NaOH to black liquor would be expected to decrease the solubility of carbonate and sulfate. This was verified directly during the solubility study. Addition of NaOH to a saturated liquor does cause additional Na_2CO_3 and Na_2SO_4 to precipitate.

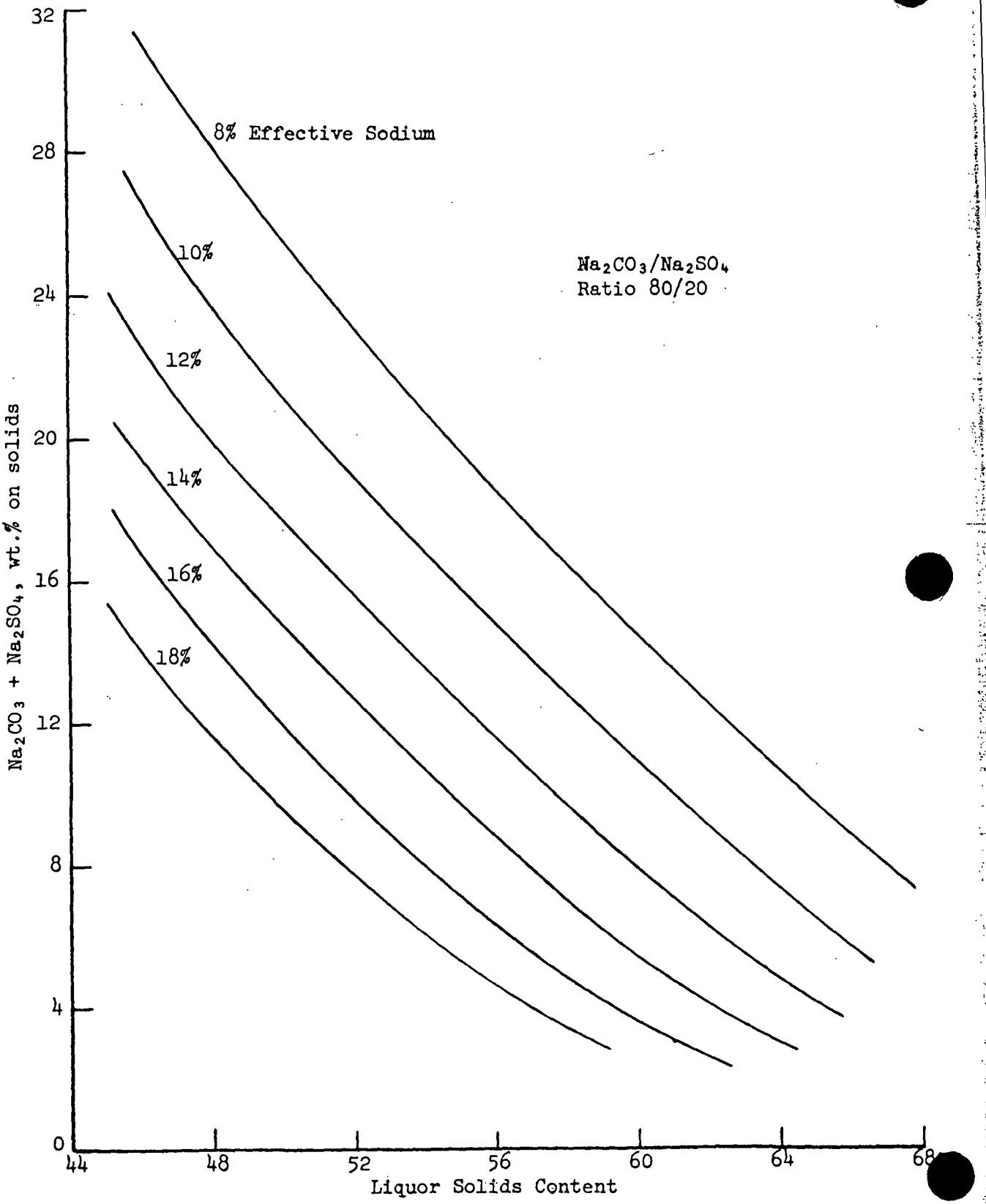

Figure 1. Correlation of Na_2CO_3-Na_2SO_4 Solubility in Black Liquor

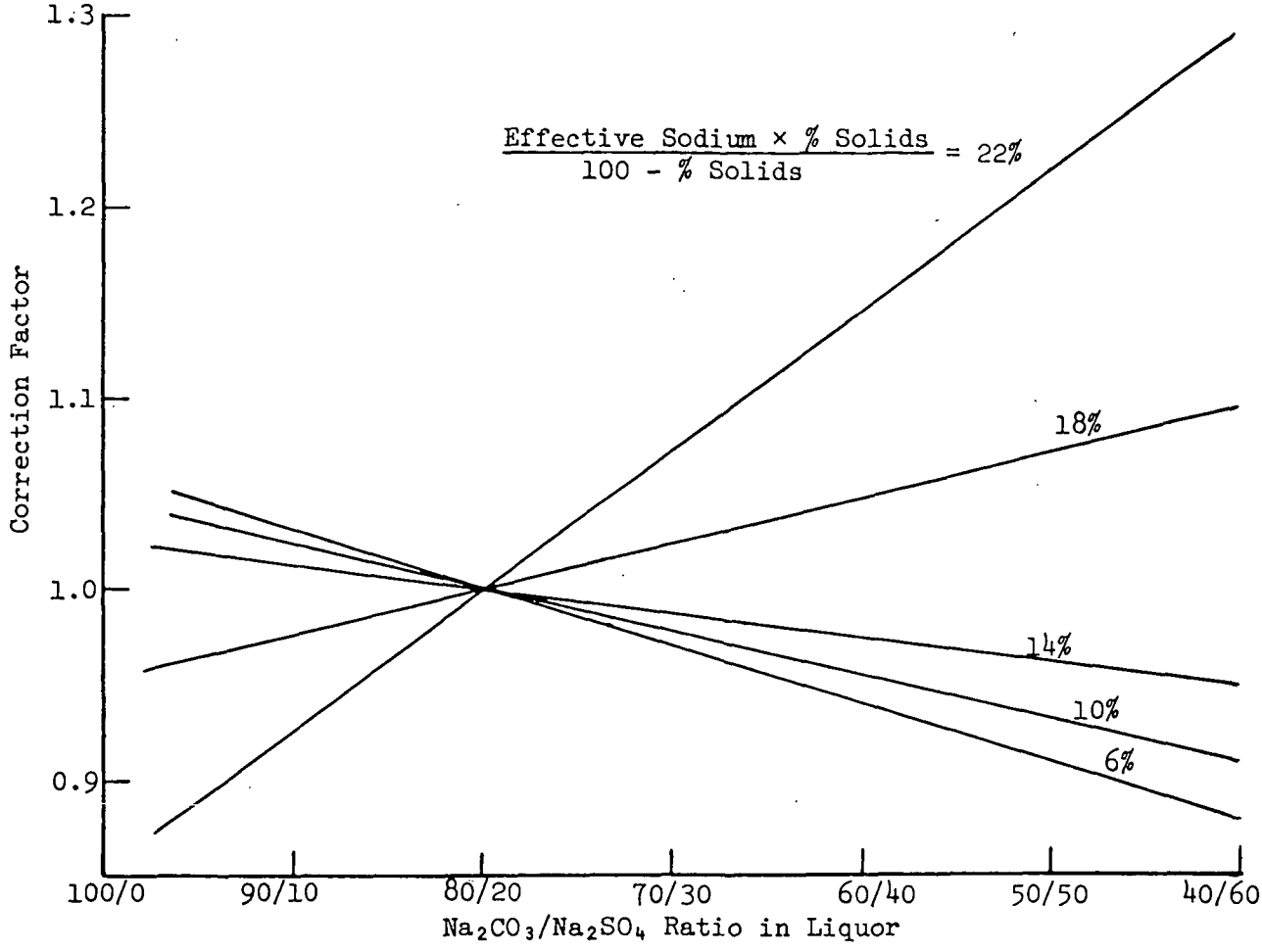

Figure 2. Correction Factor for Solubility Correlation

SOLUBILITY OF ORGANICS

Particular attention was paid to the solubility of organic constituents in the liquor. In essentially all of the solubility experiments carried out in Project 3136 and in subsequent work, the organic content of the precipitated solids was quite small. The organic which did precipitate correlated with the residual soap in the liquor. There was no evidence of lignin precipitation simply by concentrating liquors up to 65% solids. Lignin precipitation could be induced by lowering the pH of the liquor. This latter behavior could be reversed by addition of caustic to the liquor.

The solubility study strongly indicated that the major components of soluble scales should be precipitated Na_2CO_3-Na_2SO_4 containing 60-80% Na_2SO_4. This was in agreement with the findings of Dedricks and Hedstrom (5) and Stacie and Wilhelmsen (6). The solubility study also suggested that organic compounds would not be a significant component of the scale unless soap removal was poor, or the liquor pH was too low for lignin stability. In addition, the carbonate-sulfate saturation curves which were generated provided a means for a quantitative treatment of soluble scale as a crystallization process.

REVIEW OF SURVEY INFORMATION

As mentioned previously, a survey of evaporator scaling problems in the alkaline pulp industry was carried out in an earlier phase of this project and the results presented in Progress Report One (1). A questionnaire was used to obtain data on evaporator performance, cleaning frequencies, scale composition, evaporator design parameters, operating variables, and mill process conditions. This information was complemented by data on liquor composition obtained by analysis of liquor samples which were submitted by some of the mills. Of the 46 alkaline pulp mills which returned questionnaires, 28 also supplied liquor samples. In view of the importance of this survey in defining the nature and severity of evaporator scaling problems and the relevance of this information to the understanding of soluble scales, it is appropriate to review the main findings.

Data defining the extent of scaling problems encountered are presented in Table I. This includes information on cleaning frequencies and capacity loss as well as the types of scales encountered. Eighteen mills reported carbonate-sulfate scale. Evaporator operating data are given in Table II. Mills 1 through 28 are those for which liquor composition data are available. Composition information is presented in Table III. These data which are summarized here are described in detail in Progress Report One.

Statistical analysis of the data obtained in the survey showed significant correlations between the measured calcium content of the liquors and the frequency of water boilout, the rate of decline in evaporator productivity, and average heat transfer coefficients. This was interpreted to mean that calcium scales constitute the most serious scaling problem and have the strongest influence on evaporator performance. It also suggested that calcium scales,

TABLE I

DATA ON EVAPORATOR SCALING

Mill No.	Water Wash (Boil Out) Frequency, times/mo.	Acid Cleaning Frequency, times/mo.	Mechanical Cleaning Frequency, times/mo.	Production Loss Between Cleanings, %	Rate of Production Decline, %/mo.	Reported Scale
1	12	3.5	0	7.0	109	Calcium scale 1C & 1AB
2	15	1.15	0	6.5	105	Calcium carbonate, last effect scale greatest
3	7.5	0.17	0.17	30.9	241	Calcium carbonate 87%
4	2.45	2.2	0.03	26.4	124	Calcium and carbonate-sulfate scale, first effects
5	9	0	0.21	15.2	140	$CaCO_3$, 75%. 1A, 1B & 2 effects
6	6	0.67	0	--	--	Carbonate-sulfate scale, aluminum silicate scale, 1A, 1B, 2 & 3 effects
7	8.6	0.03	0.02	--	--	Calcium & silica scale. 60% CaO, 20% SiO_2, 1, 2, 3 & 4 effects
8	5	0.04	0.04	19.0	96.5	Na_2CO_3-Na_2SO_4 scale, 75%
9	5	0.06	0.17	--	--	Calcium carbonate and fiber 2B effect
10	4	0.03	0	22.1	89	Carbonate-sulfate scale and organic 2 effect starts to scale first
11	5.45	0	0.08	2.7	15	Carbonate-sulfate scale, 3 body
12	2	0	0.08	27.4	57	Fiber, Fe & alumina. Most scale can be removed by water washing. 1 & 2 bodies
13	1.33	0	0.17	24	36	Carbonate-sulfate, calcium, & fiber-dried liquor. Bottom of 1 effect
14	3.75	0.04	0.17	--	--	No composition. 1 & 2 effects, more toward top
15	0.8	--	--	10	8	Carbonate-sulfate, calcium, silica & aluminum silicate scale
16	1.6	0.04	0.04	14.8	25	Calcium carbonate. Not having an abnormal scaling problem
17	4	0.08	0.08	4.6	19	No information on scale. "We know of no scale problems"
18	3.5	0	0.02	--	--	Silica. Primary scale buildup is considered to be organic. 1 effect
19	2	0	0	--	--	Calcium scale, some silica. 1 effect
20	1	0.01	0	--	--	Na_2CO_3-Na_2SO_4 scale, no analysis, water washable. 1, 2 & 3 effects
21	0.57	0	0.055	--	--	Carbonate-sulfate & calcium scale. 2 & 3 effects, full tube length
22	0.8	0.11	0	--	--	Carbonate-sulfate scale, from appearance 1 & 3 effects
23	1.5	0.017	0.017	22.8	35	Composition not available. 3, 4 & 5 effects
24	1	0.02	0.08	20.2	22	No known scale
25	--	--	--	--	--	Scaling not a problem at this time
26	1.2	0	0	--	--	No scaling problems
27	0.8	0	0	--	--	Slight but insignificant scale in final pass of 1 effect
28	0.33	0	0	--	--	Only vapor side scale
29	6.5	0.3	--	--	--	Calcium scale primary, carbonate-sulfate secondary
30	6	0	0.04	21.4	129	Aluminum silicate scale. 1B, 1A, 2 & 3 effects
31	4.7	0	0.08	17.8	85	Carbonate-sulfate scale, worse in hot effects
32	--	--	--	--	--	$CaCO_3$ scale, up to 40% fiber
33	15	0	0	--	--	Calcium & sodium scale. Bottom of 2 effect (highest solids)
34	4	0.033	0	26.9	108	Reports silica but analysis suggests $CaCO_3$, Na_2CO_3 & Na_2SO_4, 1 & 2 effects
35	5	0.055	0.016	8.2	42	Scaling not a problem. Primarily in 1 & 2 effects but some in all
36	4	1.33	0	4.7	25	Carbonate-sulfate, calcium & silica scale. 1, 2 & 3 effects, top third, not a major problem
37	4	0.17	--	6.1	25	Carbonate-sulfate. Found in all bodies except feed bodies, increases with temperature
38	3.3	0.02	0.08	--	--	Ligneous carbonate with some Ca and Mg
39	4	0	0.04	10	40	Mild carbonate-sulfate scale. No current problems
40	1	0.17	0	--	--	Carbonate-sulfate, $CaCO_3$ & $MgCO_3$. 1, 2 & 3 effects
41	--	--	--	--	--	$CaCO_3$, slight scaling in all effects. Does not cause operating problems
42	4	0	0	--	--	No scale
43	4	--	--	--	--	No information
44	2	0	0.033	--	--	No scale problem encountered since start up
45	1	0.03	--	-	--	No scale internally
46	1	0	0	--	--	No scale

TABLE II

EVAPORATOR OPERATING DATA

Mill No.	Discharge Liquor Solids Content, %	Average Heat Flux, Btu/hr/ft^2	Average Thermal Driving Force, °F	Average Heat Transfer Coefficient, Btu/hr/ft^2/°F	Saturation Temperature of Steam Supply, °F	Production Ratio, actual/design
1	42	4390	27	163	292	0.93
2	50	3800	30	127	270	0.94
3	46	4330	25.2	172	281	0.82
4	46.9	3690	25	148	281	0.94
5	44.2	2500	17.8	140	280	0.85
6	50	3310	20.4	162	290	--
7	52	3290	22	150	--	--
8	50	3270	24.8	132	312	0.915
9	45	5530	35.5	155	292	1.00
10	49.2	5350	20.3	264	280	1.22
11	57	5890	29	203	270	0.90
12	48	5300	20	265	288	1.12
13	52	--	19.8	--	--	0.92
14	50.6	3640	19	192	280	0.87
15	50	--	22.5	--	298	--
16	46.5	4500	25	180	280	0.85
17	44	6000	23	261	--	0.80
18	43	4430	26	170	310	1.00
19	54	4210	23	184	300	0.97
20	51	4270	17.8	240	281	0.96
21	50	4630	22.2	208	296	0.82
22	48	4320	19.4	223	281	1.0
23	50	4040	19	212	--	0.91
24	50	3910	18.4	213	287	0.95
25	47	--	--	--	--	0.92
26	45	5480	16.7	329	260	1.00
27	50	3770	20.3	186	285	1.00
28	53	3920	20	194	--	0.95
29	50	--	25	--	280	--
30	50	3620	21.8	166	300	0.89
31	45	5700	23.4	243	280	1.25
32	53	--	--	--	--	1.05
33	62	6000	42	143	324	1.35
34	44	5180	19	273	275	1.06
35	45	--	22.5	--	290	0.86
36	44	4040	17.5	231	280	0.93
37	45	--	--	--	300	0.92
38	49.6	5500	19	290	280	1.10
39	47	4940	23	215	296	1.37
40	48.9	--	22	--	293	0.98
41	47	6920	26	276	280	0.94
42	45	--	19.3	--	280	0.6
43	50	6250	33.8	185	280	1.0
44	50	5050	21	241	281	1.01
45	46	4950	23	215	265	--
46	50	--	17	--	260	1.58

TABLE III

BLACK LIQUOR COMPOSITION DATA

(Expressed as wt.% on liquor solids)

Mill No.	Na_2CO_3	Na_2SO_4	Residual Active Alkali (as Na_2O)	Total Sodium	Calcium	Potassium	Residual Soap	Fiber	Saturation Solids Content, %
1	8.3	1.5	4.8	17.2	0.108	2.4	0.32	0.021	56.1
2	10.5	1.0	6.35	19.6	0.102	0.88	0.47	0.052	51.9
3	10.7	4.3	5.45	19.4	0.069	1.0	0.97	0.029	49.6
4	9.1	2.6	6.5	18.6	0.030	0.93	0.55	0.022	53.2
5	6.8	2.6	5.9	17.2	0.073	2.7	0.76	0.029	56.3
6	10.3	4.1	4.25	18.9	0.017	0.80	0.58	0.028	51.4
7	8.3	4.3	6.3	18.9	0.033	1.0	0.55	0.029	52.1
8	7.5	3.8	6.0	18.0	0.045	0.92	1.41	0.014	54.2
9	9.9	5.8	5.8	19.6	0.055	2.5	0.55	0.007	49.2
10	9.9	2.9	5.0	18.7	0.017	1.0	1.87	0.159	52.5
11	12.3	3.2	7.75	20.5	0.021	1.4	0.96	0.080	49.1
12	9.4	2.2	6.0	18.7	0.012	1.8	0.56	0.014	53.2
13	7.1	2.3	5.3	17.3	0.017	1.2	1.02	0.016	56.3
14	6.9	8.3	6.0	19.8	0.025	1.1	0.43	0.001	48.4
15	8.4	4.6	6.8	18.4	0.028	1.2	1.14	0.049	52.3
16	9.0	1.6	6.25	17.9	0.025	1.5	1.48	0.007	54.6
17	9.6	4.6	4.9	19.3	0.018	1.5	0.90	0.024	50.8
18	7.0	2.5	5.55	17.4	0.027	0.97	0.71	0.026	56.2
19	10.9	3.2	4.05	18.1	0.028	0.88	1.00	0.025	53.1
20	8.7	3.9	7.4	19.4	0.049	2.2	1.62	0.014	51.4
21	8.1	4.5	3.9	18.2	0.023	1.8	1.57	0.021	53.1
22	7.8	3.2	6.05	18.6	0.030	2.1	0.64	0.002	53.5
23	6.7	3.3	6.3	18.6	0.052	1.1	--	--	54.3
24	7.8	0.9	7.3	19.2	0.022	1.6	0.34	0.043	53.4
25	9.1	2.6	5.55	18.0	0.017	0.44	1.39	0.006	54.2
26	8.9	2.8	5.6	18.3	0.009	1.2	0.82	0.005	53.6
27	6.6	2.7	6.85	18.5	0.019	1.2	1.23	0.046	54.7
28	7.3	1.5	8.6	20.5	[illegible]6	0.86	1.33	0.028	51.9

despite their insoluble nature, could be controlled to a significant extent by water boilouts. Thus, water washing frequency is not a reliable indicator of soluble scale problems.

A somewhat surprising result of the survey was the lack of correlation between scaling indicators and those liquor composition variables (such as % Na_2SO_4, % Na_2CO_3 and saturation solids content) which would be expected to have a bearing on Na_2CO_3-Na_2SO_4 precipitation. This was attributed to the dominance of calcium scales. Although this explanation is reasonable, the observed lack of correlation between scaling indicators and carbonate-sulfate saturation could also be interpreted as meaning that soluble scale formation is not due simply to precipitation of Na_2CO_3 and Na_2SO_4 from a supersaturated solution. Since Progress Report One was published, the data have been reexamined to try to clarify this point.

The statistical correlations presented in Progress Report One were based on the full data set of all reporting mills without regard to the type of scale encountered. These correlations thus reflect the main variables controlling the type of scale having the greatest effect on evaporator performance. The strong correlation with the calcium content of the liquor indicates that these are the calcium scales. This strong dependence of scaling parameters on calcium content tends to obscure other relationships which may be involved. In order to eliminate some of this "interference" between calcium scales and soluble scales, it is helpful to divide the data set into two subsets, those mills which report having soluble scales, and those which do not. This need only be done for the twenty-eight mills which submitted liquor samples, since liquor composition data are needed to resolve the question. Mill 14 is included with the soluble scale group, even though there

were no specific data on scale composition given, because the available informati is strongly suggestive of soluble scale.

A comparison between the mills reporting soluble scale and those which did not is given in Table IV. There are some distinctive differences between these two sets of data which are most apparent in the averages. The soluble scale group is characterized by a significantly greater degree of saturation than the other group. The average concentration of Na_2CO_3 + Na_2SO_4 is 94% of the saturation level in the first case and only 81% in the second. This is definitely in agreement with the concept that soluble scales are caused by precipitation of Na_2CO_3 and Na_2SO_4 from a supersaturated solution. The greater degree of saturation in the first group is partly due to the lower average saturation solids content (the solids content at which any particular liquor become saturated in Na_2CO_3 and Na_2SO_4) for these liquors. However, the main factor is the significantly higher discharge solids levels from the evaporators (50.4% as compared to 47.6%). It is interesting to note that average amounts of Na_2CO_3, Na_2SO_4, and residual active alkali are practically the same for the soluble scale group and the group not reporting soluble scale.

These data can be interpreted as indicating that there is indeed a relationship between soluble scale formation and the solubility limits of Na_2CO_3 and Na_2SO_4 in black liquor. Soluble scales seem to form when saturation concentrations are approached or exceeded. The most important factor influencing the approach to saturation is the degree of concentration (liquor solids content reached) in the evaporator, rather than liquor composition. Soluble scales are likely to form when the evaporator discharge solids are too high, and can be avoided simply by operating at a lower final solids content.

TABLE IV

COMPARISON OF MILLS REPORTING SOLUBLE SCALE WITH THOSE WHICH DID NOT

Mill	Boilout Freq., $mo.^{-1}$	Heat Transfer Coefficient	Exit Solids, %	Saturation Solids, %	Degree of Saturation	Na_2CO_3, %	Na_2SO_4, %	Residual Active Alkali, %
				Soluble Scale Group				
4	2.45	148	46.9	53.2	0.806	9.1	2.6	6.5
6	6	162	50	51.4	0.947	10.3	4.1	4.25
8	5	132	50	54.2	0.845	7.5	3.8	6.0
10	4	264	49.2	52.5	0.875	9.9	2.9	5.0
11	5.45	203	57	49.1	1.37	12.3	3.2	7.75
13	1.33	--	52	56.3	0.842	7.1	2.3	5.3
14	3.75	192	50.6	48.4	1.092	6.9	8.3	6.0
15	0.8	--	50	52.3	0.913	8.4	4.6	6.8
20	1	240	51	51.4	0.985	8.7	3.9	7.4
21	0.57	208	50	53.1	0.883	8.1	4.5	3.9
22	0.8	223	48	53.5	0.802	7.8	3.2	6.05
Av.	2.83	196.9	50.4	52.3	0.942	8.74	3.95	5.90
				Group Not Reporting Soluble Scale				
1	12	163	42	56.1	0.566	8.3	1.5	4.8
2	15	127	50	51.9	0.928	10.5	1.0	6.35
3	7.5	172	46	49.6	0.865	10.7	4.3	5.45
5	9	140	44.2	56.3	0.608	6.8	2.6	5.9
7	8.6	150	52	52.1	0.997	8.3	4.3	6.3
9	5	155	45	49.2	0.845	9.9	5.8	5.8
12	2	265	48	53.2	0.812	9.4	2.2	6.0
16	1.6	180	46.5	54.6	0.723	9.0	1.6	6.25
17	4	261	44	50.8	0.761	9.6	4.6	4.9
18	3.5	170	43	56.2	0.588	7.0	2.5	5.55
19	2	184	54	53.1	1.037	10.9	3.2	4.05
23	1.5	212	50	54.3	0.842	6.7	3.3	6.3
24	1	213	50	53.4	0.873	7.8	0.9	7.3
25	--	--	47	54.2	0.750	9.1	2.6	5.55
26	1.2	329	45	53.6	0.709	8.9	2.8	5.6
27	0.8	186	50	54.7	0.828	6.6	2.7	6.85
28	0.33	194	53	51.9	1.045	7.3	1.5	8.6
Av.	4.69	193.9	47.6	53.2	0.811	8.64	3.71	5.97

It may be noted in Table IV that the average boilout frequency is much higher for the group not reporting soluble scale. This is due mainly to the 5 or 6 mills with severe calcium scaling problems and which have very frequent boilouts. This again demonstrates that the ability to recover evaporator capacity by boiling out with water is not a good indicator of a soluble scale problem.

This reexamination of the survey data does show the expected connection between the formation of soluble scale and the saturation concentration of Na_2CO_3 and Na_2SO_4 in black liquor. It also indicates that liquor composition is not the most important factor. The solids content to which the liquor is evaporated has a much greater influence on the approach to saturation. These facts, together with the dominant effect of calcium scales on evaporator performance, explain the apparent lack of correlation of scaling behavior with Na_2CO_3-Na_2SO_4 solubility parameters which was indicated in Progress Report One.

STUDIES WITH SINGLE-TUBE EVAPORATOR

In order to obtain data on soluble scale formation under well-defined conditions, experiments were performed on a single-tube LTV evaporator system using liquors obtained from operating kraft mills. These experiments serve as a basis for determining the factors controlling soluble scale formation and for assessing the effectiveness of control measures.

DESCRIPTION OF SYSTEM

A single-tube LTV evaporator, specially designed to permit close control of operating variables, accurate measurement of the heat transfer behavior, and easy access to the scale was used in this study. A schematic diagram of the single-tube evaporator (STE) is shown in Fig. 3. Liquor flows upward in a vertical 304 SS tube, 19 feet long by 2 inches in diameter. The shell is divided into five segments, each 3.8 feet long, to permit measurement of the heat transfer distribution along the tube.

The five major evaporator operating variables: liquor inlet temperature, inlet liquor flow, steam temperature, vapor head pressure, and inlet solids content, are all separately controlled. Heat transfer rates are measured by determining the rate of discharge of condensed steam from the shell side of the unit. Separate measurements are made of the discharge rate from each segment. An internal guard-ring arrangement is used to exclude condensate forming on the shell wall from the measurement.

A schematic diagram of the complete experimental system is shown in Fig. 4. The flow circuit includes a feed pump, flow control valve, liquor pre-heater, the single-tube evaporator itself, head pressure control valve, condenser,

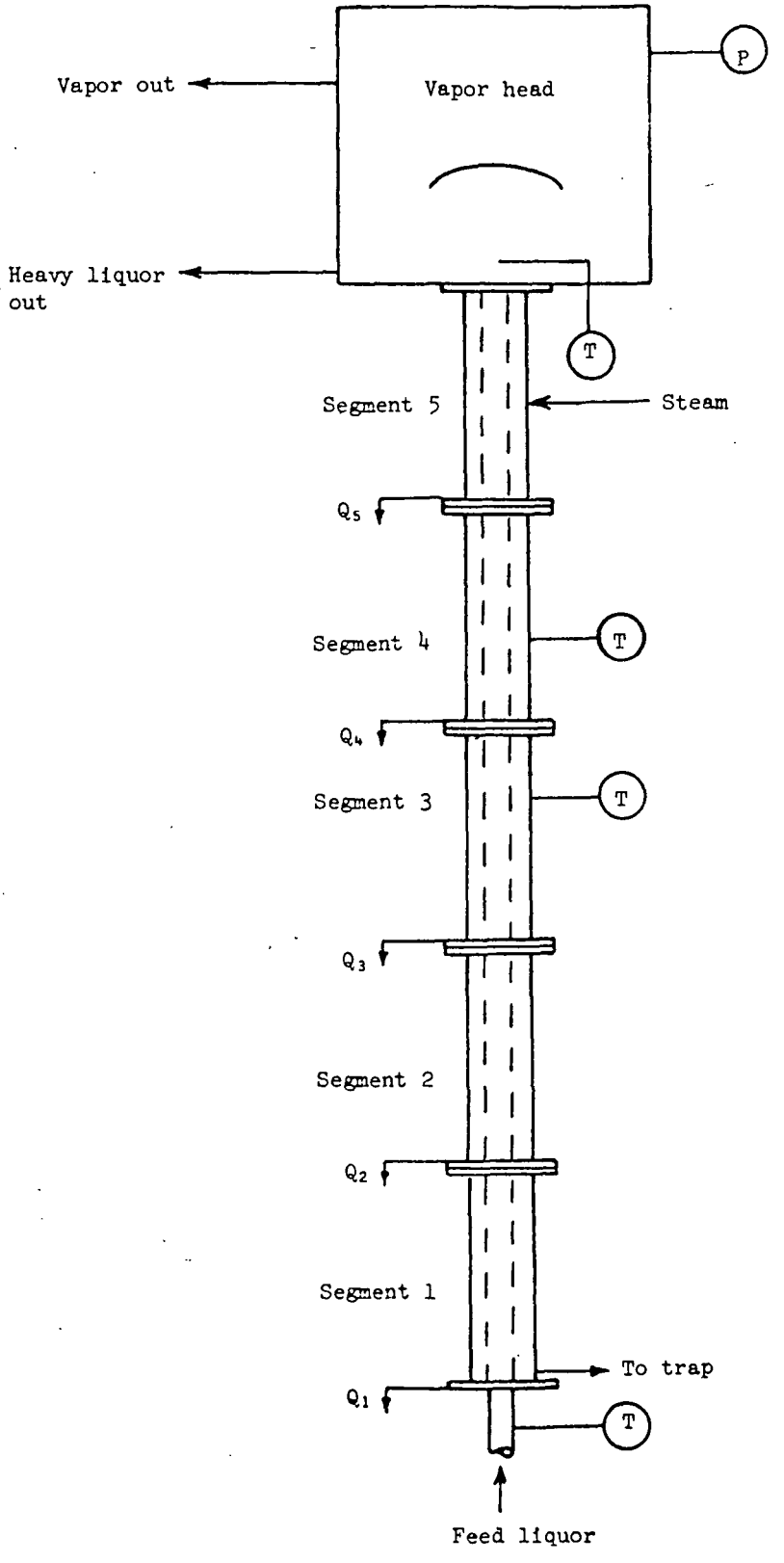

Figure 3. Schematic Diagram of Single-tube Evaporator

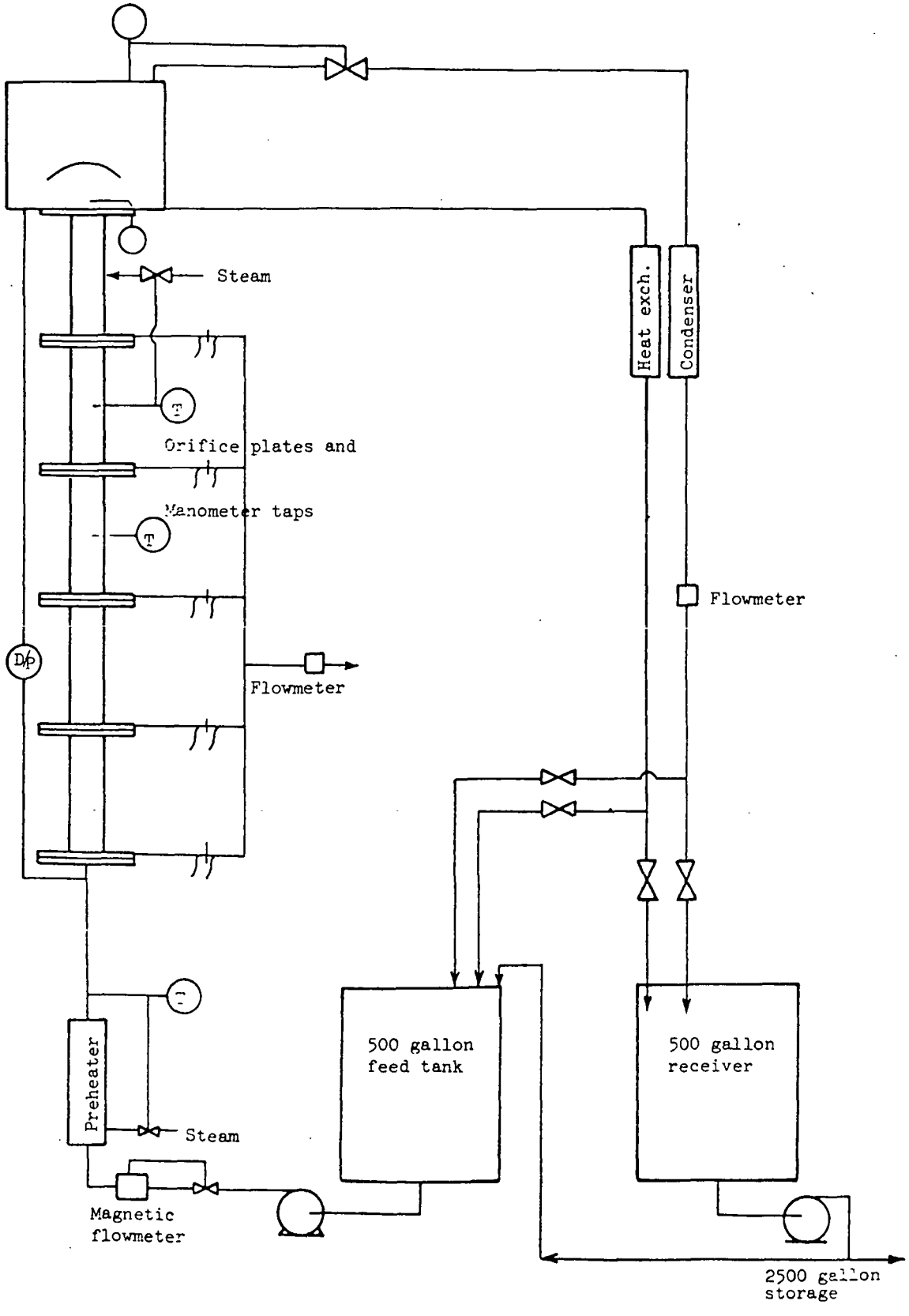

Figure 4. Schematic Diagram of Experimental System

and barometric legs for discharge of heavy liquor and condensate. Air is supplied to the vapor head to help stabilize the pressure. Two 500-gallon tanks are used as feed and receiver tanks. The return piping is such that either the heavy liquor or condensate or both can be sent directly to the feed tank. In addition, two 2500-gallon tanks are available to permit once-through operation with up to 3500 gallons of liquor.

The ranges in which the evaporator operating variables can be controlled are as follows:

Liquor Flow: 0-2.5 gpm

Liquor Inlet Temperature: 70-270°F

Steam Pressure: 5-60 psig

Head Pressure: 10 in Hg vacuum — 15 psig.

A more detailed description of the experimental evaporator system is given in Appendix I.

TYPE OF DATA OBTAINED

In order to determine the factors which govern the formation of soluble scales it was necessary to obtain data on rates of scale deposition, scale composition, and morphology, and relate them to liquor composition, evaporator operating conditions, and any other important variables.

The total amount of scale formed was found by weighing the tube before and after a run. Tubes were also sectioned and weighed to provide a direct measurement of the distribution of scale along the tube. Scale samples for analysis of composition or for morphological examination were easily obtained from the sectioned tubes.

The rate of scale formation could be monitored by observing the effect of scale on the heat transfer behavior. This provided a continuous measurement of the extent of scaling during the course of a run to complement the direct measurement of the total amount of scale formed. The rate of scale formation can be related to the overall heat transfer coefficient by

$$\dot{M} = K \frac{d}{dt}\left(\frac{1}{U}\right) \qquad (1)$$

where

$\dot{M}$ = rate of scale formation, mass of scale/unit time

U = overall heat transfer coefficient, Btu/hr ft^2 $^\circ$F

K = proportionality constant

t = time

This relationship is based on the assumption that the only effect of scale is to add an additional conduction resistance to the total heat transfer resistance and that all other heat transfer resistances are unaffected by scale growth. The overall heat transfer resistance is usually written as

$$\frac{1}{U} = \frac{1}{h_L} + \frac{\delta_w}{k_w} + \frac{1}{h_c} + \frac{\delta_s}{k_s} \qquad (2)$$

where

h_L = liquor side film coefficient

δ_w = tube wall thickness

k_w = thermal conductivity of wall

h_c = condensing side film coefficient

δ_s = scale thickness

k_s = thermal conductivity of scale

Thus, the relationship between scaling rate and overall heat transfer coefficient given in Equation (1) is valid only if the scale resistance increases linearly with scale thickness (k_s = constant) and h_L and h_c remain constant. The most questionable of these assumptions is the constancy of h_L. Heat transfer coefficients are obtained for the entire evaporator as well as separate coefficients for each segment. This permits calculating an average scaling rate for the entire evaporator and local scaling rates for each segment. The latter are highly susceptible to variations in h_L.

The independent variables which define a set of evaporator operating conditions (steam temperature, liquor inlet temperature, liquor inlet flow rate, vapor head pressure and inlet solids content) are all separately measured. The heat transfer rate, which is a dependent variable, is also measured. These then permit the calculation of other operating parameters such as sensible heat load, vapor velocity, thermal driving force, etc.

Measurements of liquor composition include solids content entering and leaving the evaporator (by revised TAPPI oven drying procedure T 650, su-71), and the amounts of critical substances in the liquor. Substances considered critical for soluble scale studies include Na_2CO_3, Na_2SO_4, total Na, residual active alkali and residual soap. The history of the liquor prior to evaporation was also recorded.

Tube surface conditions can have an important bearing on scale growth, particularly in the early stages of scaling until an initial layer of scale is formed. The intention in this program was to try to hold these types of variables constant. In all of these experiments, new tubes were used as received without any particular pretreatment.

DATA REDUCTION

All information on evaporator operating conditions and performance was obtained by measuring key variables at discrete time intervals during the run. These key variables were the elapsed time, the total pressure at the evaporator inlet and the pressure drop over the evaporator, steam pressure and temperature, liquor inlet temperature, temperature of boiling liquor leaving the tube, flow of concentrated liquor being discharged, flow of condensed vapor being discharged, total steam condensate flow, steam condensate flow from each segment and oven-dried solids contents on samples of liquor entering and leaving the evaporator.

A computer program was used to reduce these raw input data and give the desired information. Details of data reduction procedures are provided in Appendix II. A sample of reduced output data is given in Table V. For each time interval, reduced data include the variables defining the evaporator operating conditions (head pressure, steam pressure, inlet liquor flow, inlet liquor temperature and inlet solids content), the overall heat transfer behavior, the length of the evaporator tube used to supply the sensible heat load (L_s), pressure and temperature profiles along the tube, heat transfer rates and heat transfer coefficients for each segment, and information on overall heat and mass balances. All variables listed in Table V are defined in Appendix II.

The flow rate of liquor into the evaporator is computed from the measured heavy liquor flow rate and the measured solids contents of liquor entering and leaving the evaporator, rather than the magnetic flowmeter reading. This was due to the fact that the magnetic flowmeter was not very accurate at the low flow rates used. Heat transfer coefficients for each segment are based on a calculated temperature profile which takes into account the changing pressure and solids

TABLE V

SAMPLE OF REDUCED DATA OUTPUT

RUNNING TIME = 1200. MIN.

HEAD PRESS = 11.75 PSIG STEAM PRESS = 44.00 PSIG FLOW = 1140.2 LB/HR
INLET TEMP = 237.0 F SOLIDS IN = 45.3

QT = 63953. BTU/HR UT = 191.BTU/HR/FT2/F 1/UT = 0.52369 X 10**-2

SOLIDS IN VAPOR HEAD = 47.2 BY HEAT BALANCE
SOLIDS OUT OF EVAPORATOR = 47.5

TSA = 291.6 F TS = 291.3 F TVH = 257.9 F
DELTA T = 33.7 F INLET SUBCOOLING = 20.9 F

L* = 8.59 FT T* = 259.8 F P* = 13.44 PSIG IN SEGMENT 3

POSITION	0	1	2	3	4	5
P,PSIG	17.83	15.89	13.94	12.98	12.37	11.75
SOLIDS,	45.3	45.3	45.3	45.9	46.7	47.2
TL,F	237.0	245.4	255.2	259.4	258.8	257.9
TB,F	268.9	265.4	260.7	259.4		
BPR,F	13.9	13.9	13.9	14.3	14.8	15.1

SEGMENT	1	2	3	4	5
Q,BTU/HR	8136.	9497.	17073.	17460.	9702.
U, BTU/HR/FT2/F	81.2	115.7	264.0	270.0	146.7
UB,BTU/HR/FT2/F	167.4	167.2	269.9		
1/U X 100	1.23133	0.86399	0.37882	0.37034	0.68158
1/UB X 100	0.59752	0.59792	0.37057		

QSUM = 61868.BTU/HR QT = 63953.BTU/HR PERCENT ERROR = 3.3
FLOW,LB/HR WLOUT = 1087.3 WVOUT = 39.7 VENT = 13.1 TOTAL = 1140.2

concentration (boiling point rise) along the tube as well as the measured temperatures of the liquor entering and leaving the tube. Details of the calculation procedure are given in Appendix II.

EXPERIMENTAL

The formation of soluble scale was studied in a series of six experimental runs with the single-tube evaporator system. Summary descriptions and objectives of each of these runs are given below. Detailed descriptions of the experiments and the results then follow. In all cases, new 304 SS tubes were used so as to eliminate tube surface conditions as a variable in these experiments.

EXPERIMENTS PERFORMED

Experiment 1: This was a preliminary experiment designed to obtain a general understanding of the behavior of soluble carbonate-sulfate scales and to determine the relationship between scale formation and the degree of saturation of carbonate and sulfate in the liquor. The liquor used was a hardwood liquor fortified with the Na_2SO_4 and Na_2CO_3 to increase the scaling tendency. The liquor was concentrated in a series of steps until severe scaling was encountered.

Experiment 2: This experiment was carried out with a softwood liquor from a mill which was experiencing soluble scale problems. The liquor was obtained from the feed to the second effect, and the conditions used in this experiment were chosen to simulate those in the second effect of the commercial system. A major objective was to determine if deposits would form at liquor solids contents well below the critical solids content for Na_2CO_3-Na_2SO_4 precipitation. In addition, the experiment served to concentrate the liquor from the 26.7% solids at which it was obtained to 33.2% solids for subsequent runs at higher solids levels.

Experiment 3: This experiment was a sequel to Experiment 2 and was designed to obtain data on the formation of soluble scales and to relate scaling behavior to the solubility limits of Na_2CO_3 and Na_2SO_4 in the liquor. Operating

conditions were chosen to be similar to those encountered in the first effect of a conventional evaporator system. A point of interest was to determine if there were any significant differences in the scaling behavior of this liquor (known to exhibit soluble scaling tendencies in the field) and that shown by the artificially enhanced liquor used in Experiment 1.

Experiment 4: This experiment was designed to determine if the addition of caustic to the liquor would have a beneficial effect in minimizing soluble scale. A portion of the liquor from Experiment 2 was treated with an amount of NaOH equivalent to 5% on the solids (as NaOH). Operating conditions were the same as those used in Experiment 3. The system was operated with the concentrated liquor returned to the feed tank to give a gradual rise in inlet solids content. The relationship between the onset of scaling and solubility limits of Na_2CO_3 and Na_2SO_4 in the caustic treated liquor was determined.

Experiment 5: This experiment was designed to examine the effect of fiber in the liquor on scale formation. The objective was to determine if the presence of fiber caused scales to form when the bulk liquor concentration was significantly less than the saturation concentration. Fiber was added to a fresh portion of liquor from Experiment 2 in an amount equivalent to 3 lb/(1000 gal of 16% solids liquor). Operating variables were similar to those used in Experiment 4.

Experiment 6: This experiment was designed to determine if operation at higher liquor flow rates and with less sensible heat demand would permit operation, without scaling, at solids levels greater than the critical solids level. The objective was to determine if evaporator operating variables had any significant effect on scaling other than their effect on local bulk solids levels.

The liquor used was a portion of that concentrated in Experiment 2. Operating conditions were chosen to give a flow rate about three times that used in other experiments and an inlet liquor temperature as close as possible to the discharge temperature.

Experiment 1

This experiment was designed to obtain a general understanding of the behavior of the soluble sulfate-carbonate scales and to obtain quantitative data on the relationship between scale formation and the saturation limits of carbonate and sulfate. The liquor used was an all-hardwood kraft liquor fortified with Na_2CO_3 and Na_2SO_4 to enhance the scaling tendency. The original liquor had been used previously in experiments on calcium scales (to be discussed in a separate report) which had effectively depleted it of scalable calcium. This was fortified by the addition of 100 lb of Na_2CO_3 and 75 lb of Na_2SO_4 to 450 gallons of 33% solids liquor. The composition of the modified liquor (relevant to soluble scale) is given below as wt.% on an o.d. solids basis.

Na_2CO_3	14.5%
Na_2SO_4	6.2%
Residual Active Alkali (as Na_2O)	3.0%
Total Sodium	20.2%
Saturation Solids Content	47.1%

The value for the saturation solids content was taken from the general solubility correlation given in Fig. 1 and 2. The run on the single-tube evaporator is most easily described by considering it to consist of three distinct parts.

Description of Run

1. The evaporator was operated in a full recirculation mode with 450 gallons of fortified liquor for about a 24-hour period. Both the condensed vapor and concentrated liquor were returned to the feed tank to permit operation at a fixed inlet solids content over a fairly long time period with the relatively small amount of liquor available. Evaporator operating conditions, after an initial period of adjustment, were maintained as constant as possible.

2. Fifty pounds of caustic were added to the liquor to increase the residual active alkali. The important composition variables of the liquor after caustic addition were as follows:

Na_2CO_3	14.2%
Na_2SO_4	6.0%
Residual Active Alkali (as Na_2O)	5.2%
Total Sodium	21.9%
Saturation Solids Content	45.4%

Following caustic addition, operation continued essentially as in the first part of the experiment for about 6 hours. Then the condensed vapor was diverted from the feed tank to cause a slow rise in the solids content of the evaporator feed. This was continued until the feed liquor reached 36.6% solids at which time the condensed vapor flow was returned to the feed tank. Operation continued in a full recirculation mode for another three hours. Steam pressures were adjusted slightly upward as needed to maintain an overall heat transfer rate of 70,000 Btu/hr.

3. At this point in the experiment (40 hours from start) the condensed vapor was again diverted from the feed tank and the system operated in a concentrating mode. This was continued for about 12 hours until the inlet solids reached

42.2%. At that point the condensed vapor was again returned to the feed tank to maintain the feed solids at about 42.2% for the duration of the run. Heat transfer coefficients decreased significantly as the solids levels increased and the evaporator began to scale rapidly. Steam pressures were increased as needed to maintain as constant a heat transfer rate as possible.

Data

Data describing evaporator operation and the heat transfer behavior during this experiment are given in Table VI. These data include the elapsed time from the start of the run, the pressure in the vapor head, steam pressure, the overall temperature driving force (ΔT, the difference between the saturated steam temperature and the liquor boiling temperature) the subcooling (ΔT_{sc}, the difference between the liquor boiling temperature and the liquor inlet temperature), liquor flow rate, and the solids content of the inlet liquor. These data are essentially under the control of the operator and define the conditions under which the evaporator is operating at a particular time. The remaining variables are dependent on the performance of the evaporator. These include the discharge solids content, the overall heat transfer rate and overall heat transfer coefficient, and heat transfer coefficients for each of the individual segments, U_i. The latter are calculated from an assumed liquor temperature distribution along the tube as described in detail in Appendix II.

Two values of outlet solids content are given in Table VI. The first is the percentage solids of the liquor being discharged from the evaporator system as determined by direct measurements on samples. The second value is determined by a heat balance over the tube. The former will normally be somewhat low because some vapor condenses on the inside of the vapor head and dilutes the liquor being discharged. There is also a holdup in the liquor discharge piping which can cause

TABLE VI

EVAPORATOR OPERATING CONDITIONS AND PERFORMANCE DATA FOR EXPERIMENT 1

Time, hr	Pressure in Vapor Head, psig	Steam Pressure, psig	Overall ΔT, °F	ΔT_{sc}, °F	Flow, lb/hr	Inlet Solids, %	Discharge Solids, %	Solids by Heat Balance, %	Heating Rate, Btu/hr	All in Btu/hr ft² °F					
										U_p	U_1	U_2	U_3	U_4	U_5
0.75	10.0	24.5	18.3	17	295	33.8	41.6	42.8	63,400	349	217	421	412	393	406
2.25	9.75	25	18.9	20	299	33.8	42.1	43.2	67,500	359	179	402	379	364	348
3.75	10.0	24.8	18.3	20	270	33.9	42.3	43.7	62,300	343	180	341	411	380	371
5.25	9.88	27	20.6	20	287	34.0	45.2	45.8	75,700	369	217	383	378	355	358
6.75	9.5	27	21.8	25	264	34.1	44.1	46.3	72,400	334	159	363	352	333	325
8.25	10.0	27	20.9	23	263	34.0	43.8	46.0	70,700	340	140	379	371	348	318
9.75	10.25	26.8	20.4	21	263	34.0	45.1	46.3	71,300	351	156	381	421	351	320
11.25	9.63	26.6	20.3	21	257	33.3	44.6	45.3	69,700	344	172	377	421	357	327
12.75	9.5	27	20.8	23	248	34.3	45.2	48.5	74,100	358	150	351	405	338	310
14.25	10.0	26.7	19.9	16	242	34.0	43.8	47.5	69,100	349	185	392	417	338	317
15.75	9.88	27	20.8	22	241	33.6	44.3	47.3	71,300	345	155	359	415	338	306
17.25	9.75	27	21.1	24	266	33.5	43.6	44.8	69,500	332	116	440	412	343	313
18.75	10.0	26.8	20.9	24	253	33.6	43.0	46.0	70,400	339	137	329	421	349	308
20.25	9.88	28	22.0	23	257	33.7	45.1	46.7	73,300	335	132	362	414	331	300
21.75	10.0	28	21.6	26	248	33.7	44.4	46.6	71,300	332	128	343	406	336	309
23.25	9.5	27.5	21.4	21	247	33.8	44.9	47.6	72,800	342	143	368	411	339	330
24.75	10.0	27.6	21.6	24	278	33.6	44.5	44.8	72,100	336	124	354	427	348	329
25.5	Caustic added to liquor in feed tank														
26.25	10.0	27.9	21.4	22	260	34.0	45.1	47.1	74,000	347	133	362	427	354	319
27.5	9.88	27.8	20.5	19	263	33.2	44.6	45.3	71,400	350	269	466	397	345	311
29.25	9.75	27.6	20.3	21	248	33.4	44.4	46.5	71,000	351	202	399	374	350	303
30.75	9.88	27.8	20.4	21	248	33.4	45.0	46.4	70,900	349	179	397	369	356	319
32.25[a]	9.75	27.6	20.7	15	225	33.8	44.8	49.7	71,600	348	218	367	383	313	289
33.75[a]	9.88	28.0	20.5	24	239	34.7	46.2	48.9	71,100	348	141	356	382	315	283
35.25[a]	10.13	28.0	19.7	21	250	35.3	46.0	48.2	68,200	348	169	360	408	321	289
36.75[a]	9.75	29.0	20.7	26	257	36.3	48.6	49.9	72,600	353	162	363	405	317	284
38.25	9.63	29.0	19.9	25	256	36.6	48.1	49.9	70,900	358	179	387	417	345	292
39.75	9.88	29.0	20.1	26	257	36.7	48.3	49.5	69,000	346	148	360	396	317	292
	Final Phase of Experiment Initiated														
41.25[a]	9.75	29.0	20.4	25	248	37.1	47.9	49.7	65,300	321	156	379	387	312	274
42.75[a]	9.88	29.0	20.3	28	283	38.1	48.6	48.5	64,600	319	123	319	387	299	267
44.25[a]	10.0	29.0	19.8	26	264	38.6	48.6	50.3	64,400	327	144	307	381	308	286
45.75[a]	9.75	29.0	19.4	26	262	39.5	49.2	51.2	62,800	325	133	276	383	314	279
47.25[a]	10.13	29.5	20.0	27	277	40.3	48.9	50.6	60,000	302	132	264	382	304	268
48.75[a]	9.75	29.2	19.0	26	267	40.9	50.1	50.7	55,000	291	146	257	399	340	274
50.25[a]	9.63	32.0	23.5	25	274	41.8	50.3	51.3	54,200	232	127	302	356	239	80
51.05[a]	10.63	34.8	25.1	30	263	42.1	49.8	52.6	56,600	227	154	373	392	226	63
51.75[a]	9.63	36.5	29.1	25	262	42.2	51.1	54.5	62,100	215	145	325	317	83	43
52.25	9.88	36.3	28.9	26	252	42.2	50.6	52.6	52,900	184	127	322	301	99	65
52.75	9.88	43.3	35.4	31	242	42.3	52.5	57.3	66,700	189	189	350	211	68	38
53.25	10.13	42.2	35.8	26	252	42.3	50.8	52.8	53,200	149	209	314	79	72	45
53.75	9.63	48.5	42.1	30	240	42.2	52.0	55.9	62,400	149	233	270	93	47	40
54.25	10.0	48.5	42.1	29	240	42.3	51.9	55.3	59,700	143	223	248	100	57	29

[a]Denotes evaporator system operating in a concentrating mode.

the measured discharge liquor to lag behind the conditions at the tube exit. The solids determined by heat balance would be a more reliable indication of the actual solids content of the liquor leaving the evaporator tube. However, it is strongly dependent on accurate measurement of the liquor flow rate and the heat transfer rate. Accurate knowledge of liquor solids content is important because the degree of saturation changes so rapidly with solids content in this region.

Interpretation of Data for First 40 Hours

The interpretation of these data depends on comparisons between the rate of scale formation (estimated from heat transfer data and the amount of deposits formed) and the degree of sulfate-carbonate saturation in the liquor (which depends on liquor solids content).

The rate of scaling based on the overall heat transfer coefficient can be defined as $d/dt\ (1/U_o)$, and can be found from the slope of a plot of the inverse of the overall heat transfer coefficient vs. time. Such a plot is shown in Fig. 5 for the first 40 hours of Experiment 1 spanning the first two parts of the run. It is evident that there is some slight deterioration in the heat transfer coefficient (which could be interpreted as scaling) during the first part of the run (0-25.5 hr). The least-squares regression line for this part is also shown and has a slope of 6.4×10^{-6} ft^2 °F/Btu. At this rate it would take 18.4 days for the overall heat transfer rate to be cut in half from an initial value of 353 Btu/hr ft^2 °F.

The data in Fig. 5 show a small, but apparently real, beneficial effect of caustic addition. Using the regression lines for the first and second parts of the run as a basis, the overall heat transfer coefficient increases from 335 to 348 Btu/hr ft^2 °F, or about 4%, after caustic addition. In addition, the slope

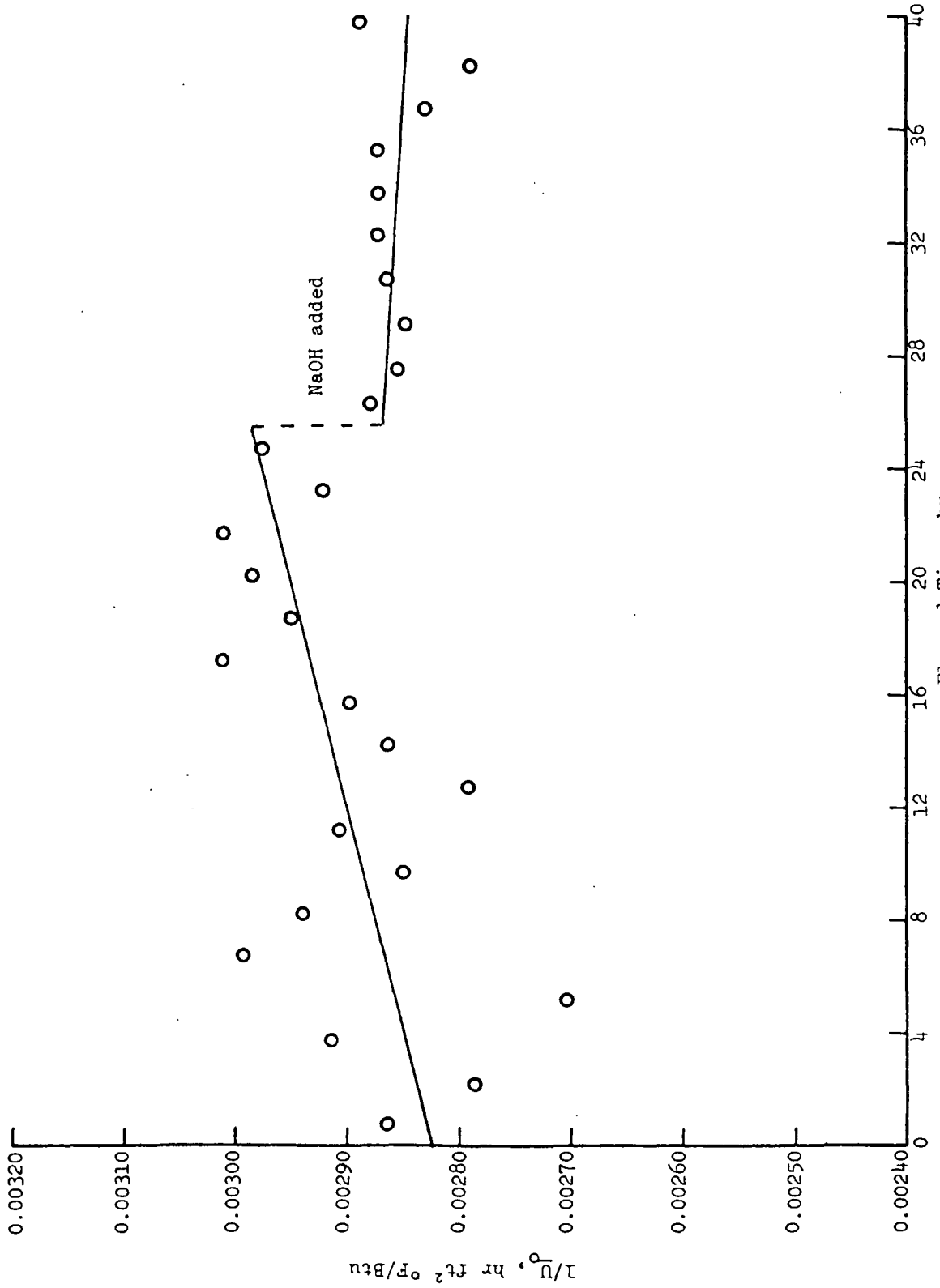

Figure 5. Overall Heat Transfer Resistance in First 40 Hours of Experiment 1

of the regression line after caustic addition is slightly negative at -1.7×10^{-6} ft^2 °F/Btu (which might be interpreted as a mild cleansing action). This effect of caustic addition was somewhat surprising since it has been established that caustic addition decreases the solubility of carbonate and sulfate in black liquor. It is, however, in agreement with a widely held view that high residual alkali levels can help to prevent scaling. For these reasons it is appropriate to examine these data in more detail and determine where "scale" is forming in the evaporator.

Scaling rates for the individual segments can be defined in a manner similar to that based on the overall heat transfer coefficient.

$$\text{Scaling rate in } \underline{i}\text{th segment} = R_i = \frac{d}{dt}\left(\frac{1}{U_i}\right)$$

Thus, the scaling rate in each of the five segments can be found from the slope of plots of $1/U_{\underline{i}}$ vs. time. Values of the regression coefficients for such plots for both parts of the run are summarized in Table VII. The results are plotted in Fig. 6. The behavior of the regression lines is more informative than plots of the actual data because of the high degree of overlap and scatter involved. Because the segment coefficients can be more sensitive to changes in operating variables than the overall coefficients, the first four points, for $\underline{t}$ = 0.75, 2.25, 3.75 and 5.25 hr (when steady operating conditions were still being established), were omitted in the determination of the regression coefficients. This does not affect the validity of the results. If the first four points were omitted from the determination of the regression lines for the overall coefficients it would result in values of 4.23×10^{-6} and 0.002865 for the slope and intercept instead of the values of 6.4×10^{-6} and 0.002823 shown in Fig. 5.

TABLE VII

REGRESSION COEFFICIENTS FOR INVERSE SEGMENT COEFFICIENTS VS. TIME PLOTS IN EXPERIMENT 1

	Before Caustic Addition		After Caustic Addition	
Segment	Slope, ft^2 °F/Btu	Intercept, hr ft^2 °F/Btu	Slope, ft^2 °F/Btu	Intercept, hr ft^2 °F/Btu
1	9.26×10^{-5}	0.005506	6.59×10^{-5}	0.003617
2	0.88×10^{-5}	0.002584	2.18×10^{-5}	0.001916
3	-1.46×10^{-5}	0.002693	-0.40×10^{-5}	0.002662
4	0.14×10^{-5}	0.002901	2.23×10^{-5}	0.002274
5	0.20×10^{-5}	0.003132	2.50×10^{-5}	0.002534
Overall (all points)	0.64×10^{-5}	0.002823	-0.17×10^{-5}	0.002915
Overall (omit first four points)	0.42×10^{-5}	0.002865		

Examination of Fig. 6 clearly shows that most of the changes occurred in the first, or bottom, segment of the evaporator. This is the region where sensible heat is supplied and forced convective heat transfer and subcooled boiling occurs. It is also the region where the liquor bulk solids content is lowest. Thus, "scaling," measured by a deterioration in segment heat transfer coefficients, is greatest where the degree of saturation in carbonate and sulfate is lowest. There appear to be several ways that this behavior might be rationalized.

1. Scaling may be caused by other materials in the liquor rather than by Na_2CO_3 and Na_2SO_4. If so, these deposits appear to be removable on exposure to higher alkali levels.

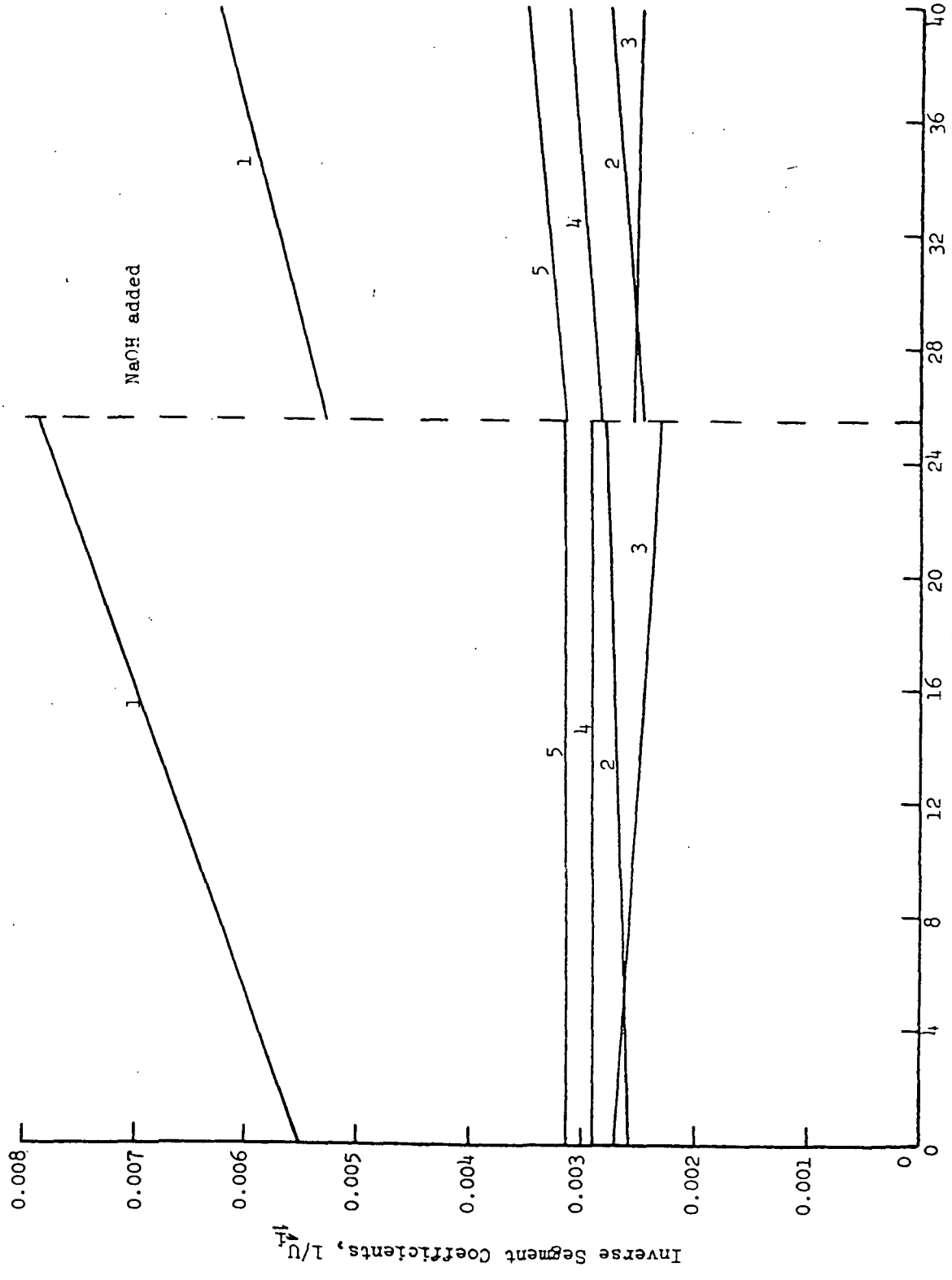

Figure 6. Inverse Segment Coefficients During First 40 Hours of Experiment 1

2. Very small amounts of deposits may have an inordinate effect on heat transfer rates by interfering with nucleation in the subcooled boiling and nucleate boiling regions of the evaporator. Palen (8) found a similar effect in his studies of $CaSO_4$ scaling during pool boiling on an electrically heated strip.

3. Sulfate-carbonate deposits might form ring-type deposits around specific nucleation sites because of local concentration due to local vaporization even though the bulk of the liquor is well below saturation.

4. The phenomenon may not be due to deposit formation at all, but rather to other phenomena (such as depletion of trapped gases or deaeration of the liquor) which would lead to a gradual deactivation of subcooled boiling. The apparent effect of caustic addition could be due to reaeration of the liquor when the caustic solution was added to the feed tank.

Although a complete explanation of these phenomena is not yet available, it is clear that these data are not in contradiction with the established fact that caustic addition lowers the solubility of carbonate and sulfate in black liquor. Bulk solubility considerations are obviously not the determining factor. Whatever the cause, the effect is quite small.

It is of interest to note that carbonate-sulfate scaling is very minor or even nonexistent in the first 40 hours of this run, even though the liquor is approaching (or possibly exceeding slightly) saturation near the tube exit. This indicates that concentration gradients between the hot surface and the bulk liquor are small and have a negligible impact on scale formation. Data on the degree of saturation (in sulfate and carbonate) existing at the discharge end of the tube are given in Table VIII. Discharge solids leaving the evaporator tube are taken

TABLE VIII

APPROACH TO SATURATION IN FIRST 40 HOURS OF EXPERIMENT 1

Time, hr	Solids at Tube Exit, %	Deg. of Satn. from General Correlation, %	Deg. of Satn. by Expt., %
0.75	43.5	92.6	80.8
2.25	44.0	94.5	82.4
3.75	44.2	95.3	83.1
5.25	47.1	107.1	93.4
6.75	46.0	102.4	89.3
8.25	45.7	101.2	88.3
9.75	47.0	106.6	93.0
11.25	46.5	104.5	91.2
12.75	47.1	107.1	93.4
14.25	45.7	101.2	88.3
15.75	46.2	103.3	90.1
17.25	45.5	100.4	87.6
18.75	44.9	98.0	85.5
20.25	47.0	106.6	93.0
21.75	46.3	103.7	90.5
23.25	46.8	105.8	92.3
24.75	46.4	104.1	90.8
26.25	47.0	106.6	93.0
27.5	46.5	104.5	91.2
29.25	46.3	103.7	90.5
30.75	46.9	106.2	92.6
32.25	46.7	105.4	92.0
33.75	48.1	111.5	97.3
35.25	47.9	110.6	96.5
36.75	50.5	122.7	107.0
38.25	50.0	120.3	104.9
39.75	50.2	121.2	105.7

Note: General solubility curve gives saturation solids content = 45.4%. Solubility measurements suggest a saturation solids content of 48.8%.

to be the measured solids of the liquor leaving the evaporator (outlet solids in Table VI) plus 1.9%. The latter is the average difference between measured outlet solids and that found by heat balance. This is believed to be a more reliable estimate of the solids content at the end of the heated section. Two values of the degree of saturation are given in Table VIII. The first is based on the saturation solids content of this liquor found from the general solubility curve (Fig. 1). The second is based on experimental measurements of the solubility of Na_2CO_3 and Na_2SO_4 in this liquor. The latter data are presented in Table IX. Values of the Na_2SO_4 + Na_2CO_3 to water ratio for the first four solution phase samples are 0.196, 0.199, 0.192, and 0.192, respectively. Assuming that the ratio 0.192 holds for the liquor in Experiment 1 containing 14.2% Na_2CO_3 and 6.0% Na_2SO_4 gives a saturation solids content of 48.8%. Using this latter estimate to determine the degree of saturation, the discharge was about 90% of the saturation concentration during most of these first two parts of the run, increasing to just over the saturation value during the latter part. This is strong evidence that the critical solids content can be approached quite closely without rapid scaling occurring.

Interpretation of Data for Final Phase

The final phase of Experiment 1 is of major interest because rapid scaling was encountered. This part of the experiment was initiated when the system was returned to the concentrating mode of operation. This caused the solids feed to the evaporator to increase from 36.7% solids to 42.3% solids over a twelve-hour period. At that point the system was switched to a full recirculation mode for the final two hours of the run.

The liquor solids contents at various positions along the evaporator tube during this final phase are given in Table X. S_{in} is the measured solids

content of the feed liquor. S_5, the solids content of the liquor leaving the evaporator tube, is equal to the measured solids content of the discharge liquor plus 1.9%. The other values, S_1 through S_4, are the liquor solids content at the end of each of the segments. These are calculated from S_{in}, S_5, and the experimental heat transfer distribution.

TABLE IX

SOLUBILITY DATA ON LIQUOR USED IN EXPERIMENT 1

	1	2	3	4	5
Solution Phase					
Total solids, %	41.7	45.4	47.2	49.9	50.3
Na_2CO_3, % on solids	20.5	17.9	15.4	14.1	12.2
Na_2SO_4, % on solids	6.9	6.0	6.1	5.2	3.6
Active alkali (as Na_2O), % on solids	4.3	4.6	4.9	4.9	5.1
Total sodium, % on solids	23.9	22.8	23.2	21.6	22.0
Solid Phase Sample					
Total solids, %	51.8	65.1	66.9	69.2	74.4
Na_2CO_3, % on solids	15.5	9.6	17.0	28.4	36.4
Na_2SO_4, % on solids	32.9	50.0	23.4	24.0	26.7
Active alkali (as Na_2O), % on solids	3.0	1.6	1.5	2.0	1.8
Total sodium, % on solids	24.2	32.3	28.2	30.2	33.0
Calculated Solid Phase					
Fraction of sample, %	17.3	36.1	37.3	38.5	48.6
Na_2CO_3, %	5.5	2.9	18.3	39.8	49.3
Na_2SO_4, %	84.7	85.4	37.1	39.0	39.0
Active alkali, %	0.1	-0.8	-0.4	-0.3	0.0
Total sodium, %	24.8	39.9	32.2	37.1	38.8

TABLE X

LIQUOR SOLIDS CONTENT PROFILE DURING
FINAL PHASE OF EXPERIMENT 1

(All values as wt.%)

Run Time, hr	Incremental Time, hr	S_{in}	S_1	S_2	S_3	S_4	S_5
41.25	0	37.1	37.7	40.5	43.8	46.9	49.8
42.75	1.5	38.1	38.3	40.9	44.4	47.5	50.5
44.25	3	38.6	39.0	41.3	44.5	47.5	50.5
45.75	4.5	39.5	39.8	41.9	45.1	48.2	51.1
47.25	6	40.3	40.5	42.4	45.4	48.2	50.8
48.75	7.5	40.9	41.2	43.0	45.9	48.9	52.0
50.25	9	41.8	42.1	44.9	48.5	51.2	52.2
51.05	9.8	42.1	42.7	45.5	48.9	51.1	51.7
51.75	10.5	42.2	43.1	46.8	51.1	52.4	53.0
52.25	11	42.2	42.8	46.4	50.1	51.5	52.5
52.75	11.5	42.3	44.0	48.9	52.4	53.7	54.4
53.25	12	42.3	44.4	49.1	50.5	51.8	52.7
53.75	12.5	42.2	45.1	49.9	51.8	52.9	53.9
54.25	13	42.3	45.1	49.7	51.8	53.1	53.8

Values of the overall heat transfer coefficient and the segment coefficients are given in Table VI. The overall heat transfer resistance, U_o^{-1}, is plotted *vs.* time in Fig. 7. It is evident that very severe scaling was encountered. The scaling rate $d/dt\ (1/U_o)$ reaches a value of about 0.001 $ft^2\ ^\circ F/Btu$ which is more than 150 times as fast as the scaling rate in the first part of the experiment. The overall coefficient is cut in half from a value of 322 to 161 Btu/hr $ft^2\ ^\circ F$ in about seven hours. Obviously scale formation is much more intensive in these last few hours of the run.

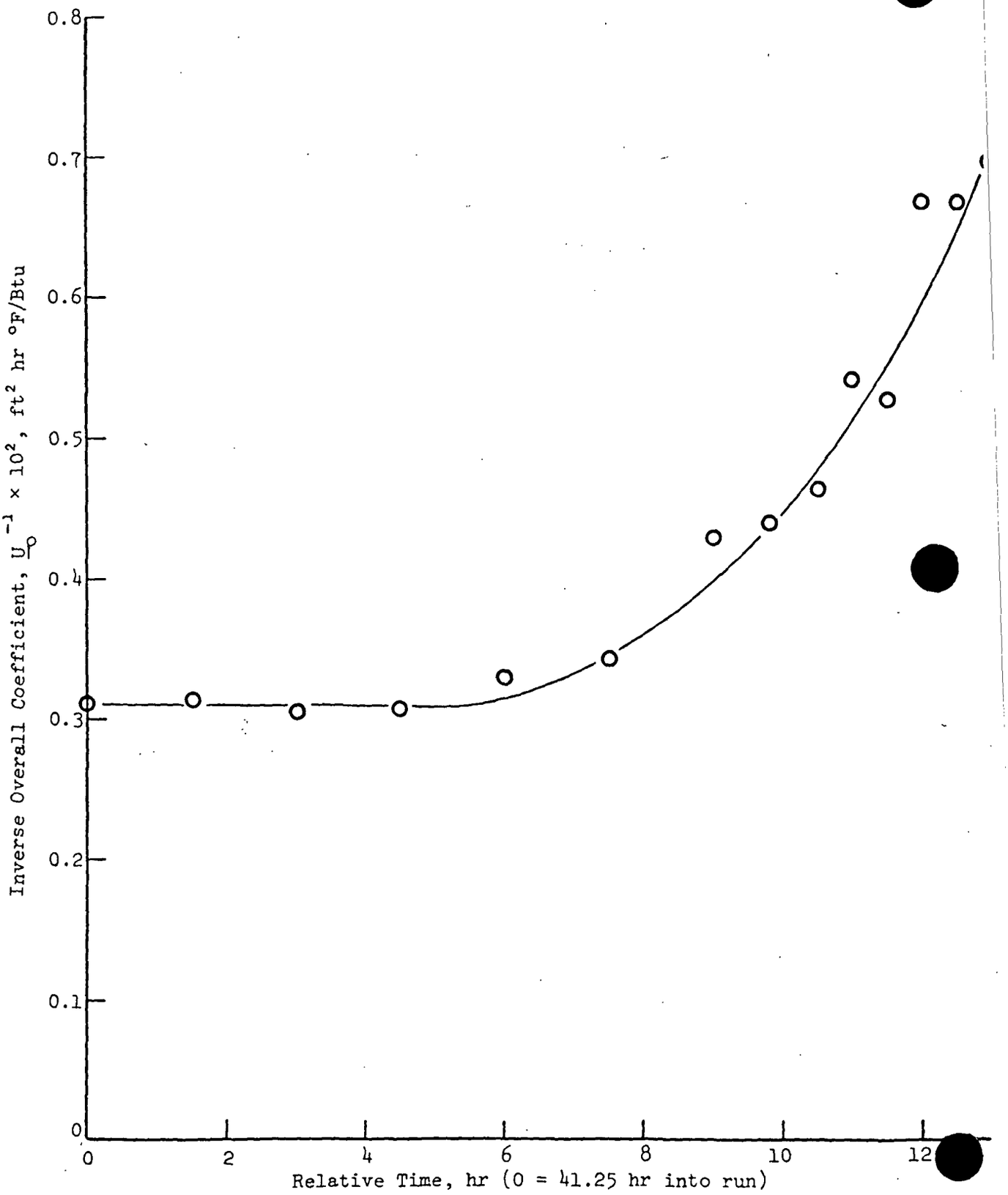

Figure 7. Overall Heat Transfer Resistance During Final Phase of Experiment 1

The extreme rapidity of the scaling process when the critical conditions for scale formation are exceeded is made evident by considering conditions in each of the five segments. Plots of $1/U_i$ vs. time for each segment are shown in Fig. 8. The onset of rapid scaling is quite abrupt. It begins at the top of the evaporator (Segment 5) and gradually works down. In Segment 5, the heat transfer resistance increases from 0.00365 to 0.0125 hr ft^2 °F/Btu in the relative time period of 7.5 hr to 9 hr. This is an increase by a factor of three in an hour and a half. The final resistance is nine times that which existed before rapid scaling began. Segments 4 and 3 also show very sudden increases in heat transfer resistance, although these are delayed in time. These data definitely show that once certain conditions are reached in the evaporator, soluble scale can form very rapidly. The rate of scaling, in the regions of the evaporator where scale is forming, is much more rapid than would be inferred from the decrease in the overall heat transfer coefficient.

The particular behavior shown in Fig. 8 is a consequence of the method of operating the evaporator during this experiment. The system was operated to try to maintain a constant heat transfer rate, and the steam pressure was increased when necessary to maintain the same overall heat transfer rate. Then, when rapid scaling developed in the top segment, the heat transfer resistance went up rapidly, and little heat was transferred in this segment. Thus, when the steam temperature was raised to maintain the total heat transfer rate constant, a greater fraction of this heat was transferred in the bottom four segments, and the region of high liquor solids shifted lower in the evaporator. Eventually the 4th segment went critical, and the process repeated itself. The shifting of the region of high solids to lower and lower positions in the evaporator is clearly evident in Table X.

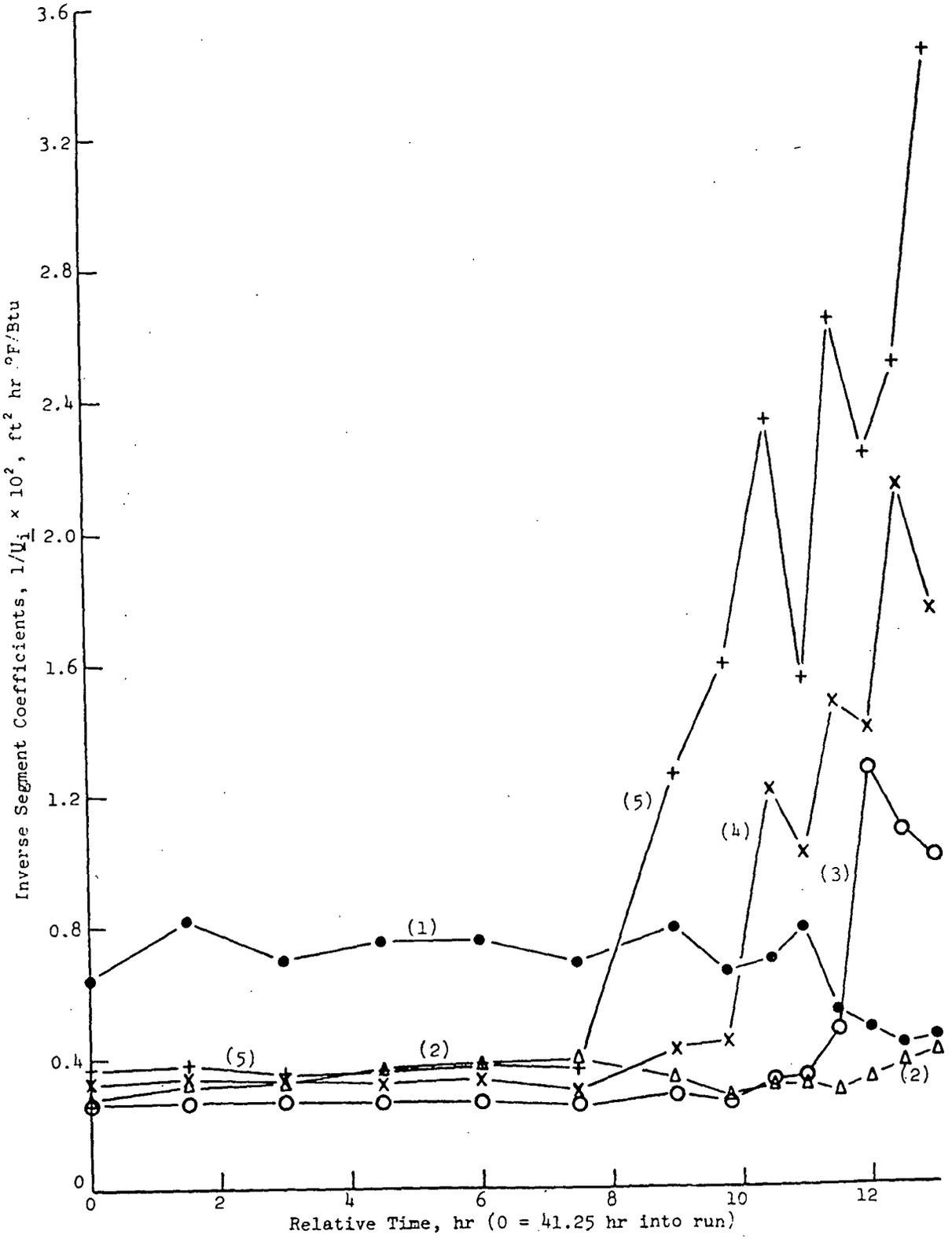

Figure 8. Inverse Segment Coefficients During Final Phase of Experiment 1

The main reason for increasing the steam temperature to maintain a constant heat transfer rate in this run was to try to maintain a constant value of the liquor side film coefficient so that changes in the overall coefficient U_o would only be due to scale. It was recognized that the boiling coefficient is a function of the temperature difference between the hot surface and the liquor. If the steam temperature was held constant, the temperature difference between the hot surface and the liquid would drop off as scale grew. Increasing the steam temperature could counterbalance this and lead to a constant temperature difference between the hot surface and the liquor. This approach did not work out very well, because scale growth was localized rather than uniform over the tube. As scale grew from the top down, local ΔT's increased in the bottom of the evaporator and decreased in the top portion. This caused changes in the heat flux distribution and flow pattern along the evaporator tube which caused changes in the liquor film coefficient with position and time. Thus, changes in the segment coefficients U_i with time represent changes in liquor film coefficients as well as scale growth. This is the reason for the oscillatory behavior of the segment resistances in Fig. 8. The dominant trend is due to scale formation. The fluctuations are due to changes in the liquor film coefficients in response to changes in steam pressure.

Scale Distribution

The amount of scale present in the evaporator tube at the end of the run was determined by weighing. The tube was sectioned to permit determination of the distribution along the tube. The data are summarized in Table XI and shown in Fig. 9. The distribution of scale found correlates well with the measures of scaling rate found from the segment coefficients. If the liquor film coefficient did not vary, the amount of scale present is just $1/U_i(t) - 1/U_i(0)$ where $t = 0$ indicates the time period before scaling began. Values of the segment coefficients

TABLE XI

WEIGHT DISTRIBUTION OF SCALE FORMED DURING EXPERIMENT 1

Position	Section Length, ft	Weight of Scale in Section, g	Cumulative Weight From Bottom, g	Cumulative Distance From Bottom, ft	Average Scale Density in Section, g/ft^2	Average Distance From Bottom, ft
Top						
15	0.99	259.6	2195	18.86	501	18.37
14	1.01	277.2	1935	17.87	524	17.37
13	1.00	264.0	1658	16.86	504	16.36
12	1.00	242.2	1394	15.86	463	15.36
11	1.01	227.2	1152	14.86	430	14.36
10	.99	205.3	925	13.85	396	13.36
9	1.01	181.5	719	12.86	343	12.36
8	.98	147.0	538	11.85	287	11.36
7	1.00	139.6	391	10.87	267	10.37
6	.99	98.4	251	9.87	190	9.38
5	.99	52.9	153	8.88	102	8.39
4	1.01	28.7	100	7.89	54	7.39
3	1.00	28.8	71	6.88	55	6.38
2	1.01	13.4	42.4	5.88	25	5.38
1	4.87	29	29	4.87	11	2.44
Bottom						

Scale in Segment 5 = 990 g
" 4 = 768 g
" 3 = 374 g
" 2 = 75 g
" 1 = 18 g

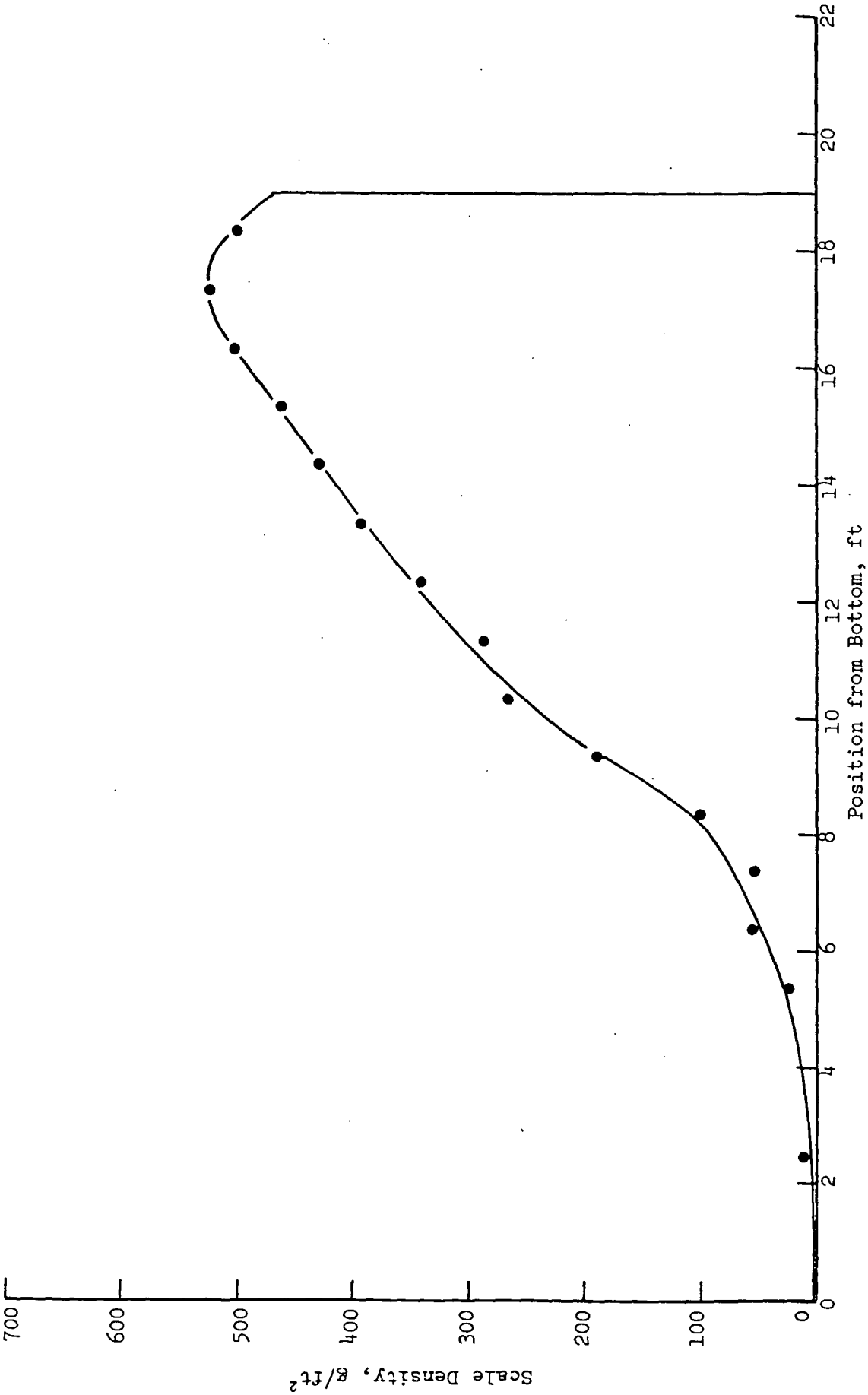

Figure 9. Scale Distribution in Experiment 1

at the beginning and the end of the final phase of Experiment 1 can be used to estimate the amount of scale present and compared with that actually found. This comparison is made in Table XII.

TABLE XII

COMPARISON OF HEAT TRANSFER RESISTANCE WITH THE AMOUNT OF SCALE FORMED

Segment	$1/\underline{U}_i(13) - 1/\underline{U}_i(0)$, ft^2 hr °F/Btu	Amount of Scale, lb	Ratio, ft^2 hr °F/Btu lb
5	3.08	2.18	1.41
4	1.43	1.69	0.85
3	0.74	0.82	0.90
2	0.14	0.165	0.85
1	-0.193	0.04	--

The ratio of the resistance increase to the amount of scale formed is nearly constant for Segments 2, 3, and 4. The ratio is somewhat higher in Segment 5 because of the variability in the liquor film coefficient and inherent measurement errors at low heat transfer rates. A different result would be obtained if the second last point (at $\underline{t}$ = 12.5) was used. No relationship was expected for Segment 1 because almost no scale is formed there, and changes in the heat transfer coefficient in that segment are due to variables other than scale formation. Thus, the measured scale distribution supports the use of inverse segment heat transfer coefficients to measure scaling rates.

Scale Composition

The composition of the scale is summarized in Table XIII. The scale is essentially a soluble sulfate-carbonate scale. The deposit is significantly richer in carbonate than it would be if it were just Burkeite ($2Na_2SO_4 \cdot Na_2CO_3$).

This suggests that under the conditions existing in the evaporator, the scale forms by simultaneous precipitation of sodium carbonate and Burkeite. This is not in complete agreement with equilibrium solubility behavior.

TABLE XIII

COMPOSITION OF SCALE FROM EXPERIMENT 1

(Data as wt.% of scale)

Carbonate as Na_2CO_3	50.2
Sulfate as Na_2SO_4	39.4
Calcium	0.35
Barium	0.18
Silica as SiO_2	0.077
Manganese	0.012
Iron	0.009
Magnesium	0.017
Aluminum	0.018
Fiber	0.18

The fact that a soluble sulfate-carbonate scale was formed suggests that there ought to be a relationship between the scaling conditions and the solubility limits of Na_2CO_3 and Na_2SO_4 in black liquor. The most direct way to find such a relationship is to examine the conditions just prior to and after the onset of rapid scaling in the segments. These are tabulated in Table XIV. It can be seen that in all cases the solids content of the liquor entering the segment reaches the saturation solids content just before rapid scaling begins. Thus, rapid scaling appears to be associated with supersaturation of the liquor throughout the segment. It should be noted that concentration of the liquor to just a few percent above the saturation solids content leads to very severe

scaling. Thus, the formation of soluble scale does exhibit a critical solids type of behavior which is very closely tied to the saturation concentration of Na_2CO_3 and Na_2SO_4 in the liquor.

TABLE XIV

CONDITIONS AT ONSET OF RAPID SCALING

	Before Onset			After Onset		
Segment	Time	Solids In	Solids Out	Time	Solids In	Solids Out
5	7.5	48.9	52.0	9	51.2	52.2
4	9.8	48.9	51.1	10.5	51.1	52.4
3	11.5	48.9	52.4	12	49.1	50.5

Potential Scale

A quantitative relationship between the rate of scaling and the saturation concentration can be found by using the concept of potential scale. Potential scale can be defined as the difference between the amount of scale-forming substance entering the evaporator and that which can leave as a saturated solution at the discharge conditions. This can be expressed quantitatively as follows.

$$\text{Potential Scale} = PS = W_{in}\, S_{in}\, C_{in} - W_o\, S_o\, C_o^* \qquad (3)$$

where

W_{in} = liquor flow into evaporator, lb/hr

W_o = liquor flow out of evaporator (or segment), lb/hr

S_{in} = solids content of inlet liquor, lb solids/lb liquor

S_o = solids content of liquor out of evaporator (or segment), lb/lb

C_{in} = concentration of scaling substance, lb/lb solids

C_o^* = saturation concentration of scaling substance at outlet conditions, lb/lb solids

Neglecting the amounts of substance being deposited (compared with the throughput rate), conservation of solids gives

$$W_{in} S_{in} = W_o S_o \tag{4}$$

The saturation concentration can be expressed on a water basis by setting

$$C_o^* = \frac{(1 - S_o)}{S_o} C_o^{**} \tag{5}$$

where C_o^{**} = saturation concentration, lb/lb water. Thus

$$PS = W_{in} S_{in} \left[C_{in} - \frac{(1 - S_o)}{S_o} C_o^{**} \right] \tag{6}$$

Equation (6) was used to calculate the potential scale in each evaporator segment during the final phase of Experiment 1. The value of C_i is 0.202 lb (Na_2CO_3 + Na_2SO_4)/lb solids and the value chosen for C_o^{**} was 0.193 lb (Na_2CO_4 + Na_2SO_4)/lb H_2O which corresponds to a saturation solids content of 48.8% for this liquor. These data are given in Table XV. Negative values of potential scale indicate the capability to dissolve that amount of scale. All values are in lb/hr, thus, potential scale is a measure of the possible scaling rate.

It is evident that positive values of potential scale existed even when a particular segment did not show evidence of rapid scaling. The onset of rapid scaling seems to correlate with a positive value of potential scale in the preceding segment. The sensitivity of potential scale to changes in liquor solids content and the relatively large magnitude of the potential scale explain why there is a critical condition for the onset of rapid scaling.

The values of potential scale can be integrated over those times when a positive value existed. This provides an estimate of the maximum amount of scale which could form. This can be compared to the amount which did form. These

are summarized in Table XVI. It is seen that only a relatively small fraction of the potential scale actually forms. This is not too surprising. The degree of supersaturation is merely the driving force for scale, and there is also a mass transfer process which can be rate limiting. As the residence time of supersaturated liquor in the tube decreases, it would be expected that a smaller fraction of the total possible scale would form. This is in agreement with the findings above, since the velocity increases rapidly from the bottom of the evaporator to the top.

TABLE XV

POTENTIAL SCALE PROFILE DURING
FINAL PHASE OF EXPERIMENT 1

(Based on saturation solids = 48.8%)

Incremental Time, hr	PS 1, lb/hr	PS 2, lb/hr	PS 3, lb/hr	PS 4, lb/hr	PS 5, lb/hr
0	-10.8	-7.50	-4.20	-1.52	0.69
1.5	-11.7	-8.29	-4.28	-1.22	1.38
3	-10.2	-7.37	-3.94	-1.15	1.31
4.5	-9.31	-6.79	-3.41	-0.56	1.79
6	-9.10	-6.72	-3.36	-0.60	1.68
7.5	-8.02	-5.88	-2.78	0.03	2.60
9	-7.26	-3.99	-0.34	2.07	2.89
9.8	-6.31	-3.23	0.04	1.92	2.40
10.5	-5.84	-1.92	1.91	2.95	3.41
11	-5.95	-2.23	1.04	2.15	2.91
11.5	-4.47	0.03	2.73	3.65	4.12
12	-2.31	0.21	1.37	2.39	3.07
12.5	-3.34	0.83	2.27	3.06	3.74
13	-3.34	0.68	2.27	3.20	3.68

TABLE XVI

INTEGRATED POTENTIAL SCALE VS. AMOUNT OF SCALE FOUND

	Segments				
	1	2	3	4	5
$\int$ PS dt, lb	0	0.88	6.2	14.0	31.6
Scale found, lb	0.04	0.165	0.82	1.69	2.18
Scale formed, %	--	18.8	13.2	12.1	6.9

Summary

This experiment showed that a soluble Na_2CO_3-Na_2SO_4 scale could form during evaporation of black liquor. The formation of this scale is very closely tied to the saturation concentration of Na_2CO_3 and Na_2SO_4 in the liquor. Liquors could be concentrated very close to the saturation limit without significant amounts of scale formed. Once the saturation concentration was exceeded, scales could form at a very rapid rate. The saturation solids content of the liquor could only be exceeded by about 1 or 2% before very severe scaling set in. This type of scaling process appears to be governed by solubility considerations in the bulk liquor, rather than by conditions (such as temperature gradients) at the wall. The existence of a critical solids content for sudden onset of extremely severe scaling is readily explained by the potential scale concept and the sensitivity of potential scale to the solids content in the evaporator.

Experiment 2

This experiment was carried out with a softwood liquor from a mill which was experiencing soluble scale problems. At the time that the liquor was obtained the evaporator set was being boiled out every five days. A total of 4000 gallons of liquor at about 27% solids was obtained for use in the soluble scale study. This liquor was taken from the feed line to the second-effect evaporator. The composition of the liquor is given below as wt.% on a dry solids basis.

Na_2CO_3	12.5%
Na_2SO_4	7.3%
Residual Active Alkali (as Na_2O)	4.8%
Total Sodium	20.5%
Saturation Solids Content	46.7%

Description of Run

The conditions used in this experiment were designed to simulate the actual operating conditions in the second effect of the mill's evaporator set. A major objective was to determine if deposits would form under controlled conditions at liquor solids contents well below the saturation solids content for Na_2CO_3-Na_2SO_4 precipitation. A secondary objective was to concentrate the liquor for later experiments at higher liquor solids contents.

All of the liquor (4000 gallons) was evaporated on a once-through basis. The condensed vapor was sewered and the concentrated liquor stored in one of the large storage tanks. The total time of the run was 67 hours. Evaporator operating conditions used during the experiment are summarized below.

Pressure in vapor head = 3.5 psig

Steam pressure = 17 psig

Overall ΔT = 24-25°F

Subcooling ΔT = 27°F

Flow rate = 1 gal/min

Inlet solids = 26.7%

Discharge solids = 33.2%

Solids by heat balance = 33.5-34%

Data

Data from Experiment 2 are presented in Table XVII. This is the same type of data that were given in Table VI in Experiment 1 and which was described at that time.

Examination of the tube after the run showed a light brown deposit which was very thin. The total weight of deposit found was 10 g (out of a total weight of tube plus deposit of 14,650 g). Separate tests have shown that tubes can be weighed to within 3 g. Thus, the small amount of deposit does appear to be real. The top 6 inches of the tube was cut off and bisected. Most of the deposit could be removed with water and is apparently dried liquor solids. In certain areas there were ring shaped, donutlike deposits. These are believed to form around specific boiling nucleation sites. After water washing the cut section, a very thin deposit remained. Energy dispersive x-ray analysis indicated this to be rich in calcium.

It seems clear that a soluble Na_2CO_3-Na_2SO_4 scale did not form during this experiment. Likewise there is no evidence for an organic deposit. There was some slight degradation in the heat transfer performance during the run. The scaling rate, based on the overall coefficient, was 3.2×10^{-6} ft^2 °F/Btu or about 1/2 the value found during the first part of Experiment 1. This is a very low rate of scaling. As in Experiment 1, most of the loss in performance appears to be in Segment 1, the subcooled zone. The same phenomenon seems to be occurring. Something interferes with subcooled nucleate boiling, and the coefficient drops toward the very low values characteristic of forced convection at the low velocities involved.

TABLE XVII

EVAPORATOR OPERATING CONDITIONS AND PERFORMANCE DATA FOR EXPERIMENT 2

Time, hr	Pressure in Vapor Head, psig	Steam Pressure, psig	Overall ΔT, °F	ΔT_{-sc}, °F	Flow, lb/hr	Inlet Solids, %	Discharge Solids, %	Solids by Heat Balance, %	Heating Rate, Btu/hr	All in Btu/hr ft^2 °F					
										U_o	U_1	U_2	U_3	U_4	U_5
1	3.25	17	24.0	27.0	501	26.3	32.9	34.5	126,800	530	——— Invalid data ———				
2	3.63	16.8	23.8	27.5	508	26.3	33.0	33.7	119,900	505	——— Invalid data ———				
3	4.5	17	23.8	28.1	509	26.3	33.2	33.7	121,100	510	156	455	553	584	539
4	4.5	17.2	24.8	28.4	501	26.3	33.2	34.4	125,900	511	256	476	553	566	547
5	4.25	17	23.9	27.7	510	26.3	33.2	33.8	121,800	509	149	463	552	574	564
6	4.0	17	23.8	27.7	518	26.3	33.4	33.6	121,300	511	152	473	560	590	569
7	3.25	17	23.9	27.7	488	26.3	33.7	34.4	122,600	515	149	502	563	582	572
8	3.38	17	23.6	29.3	487	26.4	33.5	34.4	121,600	518	153	495	567	587	578
9	3.38	17	23.5	28.1	498	26.4	33.3	34.2	121,800	521	167	486	580	599	579
10	3.88	17	23.5	27.0	496	26.4	33.1	34.3	121,800	521	169	489	562	590	578
11	3.38	16.8	23.8	28.6	536	26.4	33.0	33.3	121,500	514	159	464	595	603	582
12	3.5	17	24.0	28.1	527	26.5	33.2	33.7	122,300	512	161	480	587	600	572
13	3.5	17	24.0	27.5	524	26.5	33.5	33.8	122,300	511	159	482	579	589	573
14	3.38	17	24.1	25.7	544	26.5	33.3	33.5	122,800	512	158	476	589	600	570
15	3.50	17	24.3	28.6	538	26.5	33.1	33.6	123,300	510	154	455	582	594	564
16	3.5	17	24.1	27.5	--	26.5	33.1	--	122,100	509	——— Invalid data ———				
17	3.38	17	24.2	27.5	540	26.5	33.0	33.5	122,800	510	154	470	587	591	575
18	3.63	17.2	24.2	27.5	537	26.5	33.0	33.6	123,000	511	155	467	588	593	572
19	3.63	17.3	24.3	28.1	537	26.5	33.1	33.6	122,800	508	154	467	583	590	569
20	3.38	17	24.0	28.1	537	26.5	33.1	33.5	122,200	511	150	471	587	595	573
21	3.38	17.2	24.0	23.8	542	26.5	33.0	33.6	122,300	511	158	485	596	598	574
22	3.25	17	24.3	27.5	550	26.5	33.0	33.2	120,600	499	156	462	590	599	564
23	3.5	17	24.1	28.8	557	26.5	32.9	33.2	122,800	512	149	448	581	593	571
24	3.5	17	24.0	28.1	541	26.5	33.0	33.4	122,100	511	154	459	585	593	573
25	3.38	17	24.3	27.5	545	26.6	33.0	33.6	123,100	509	154	461	586	591	569
26	3.88	17	23.9	26.8	539	26.6	33.0	33.7	122,200	513	149	453	576	592	576
27	3.63	17	24.4	29.0	533	26.6	33.1	33.7	121,800	502	145	442	581	596	569
28	3.88	17	23.9	26.5	522	26.6	33.1	33.9	121,500	510	150	455	578	595	579
29	3.75	17	24.5	29.0	528	26.5	33.2	33.5	120,600	495	140	433	571	584	568
30	3.75	17	24.2	27.7	525	26.5	33.2	33.8	122,200	507	142	447	581	597	575
31	3.38	17.2	24.1	27.5	525	26.5	33.3	33.8	122,300	509	145	454	589	596	577
32	3.25	17	23.9	27.0	530	26.6	33.3	33.8	121,600	510	144	444	579	598	578
33	3.38	17	23.8	27.4	515	26.6	33.2	33.9	120,100	508	141	468	577	603	581
34	3.38	17	23.8	29.0	530	26.6	33.2	33.5	119,700	505	133	452	567	601	584
35	3.38	17	23.8	26.1	524	26.6	33.3	33.9	121,000	512	135	480	565	605	585
36	3.38	17	23.8	28.4	527	26.6	33.2	33.7	120,800	509	132	456	563	597	587
37	3.38	17	24.0	25.7	519	26.6	33.2	33.9	120,200	503	145	478	563	599	580
38	3.38	17	24.1	28.1	520	26.6	33.2	33.8	119,800	499	132	457	555	594	585
39	3.5	17	24.4	26.8	521	26.6	33.3	33.8	119,700	493	131	454	549	585	579
40	3.38	17	24.0	27.4	514	26.7	33.3	34.0	119,700	501	132	455	549	587	587

TABLE XVII (Continued)

EVAPORATOR OPERATING CONDITIONS AND PERFORMANCE DATA FOR EXPERIMENT 2

Time, hr	Pressure in Vapor Head, psig	Steam Pressure, psig	Overall ΔT, °F	ΔT_{sc}, °F	Flow, lb/hr	Inlet Solids, %	Discharge Solids, %	Solids by Heat Balance, %	Heating Rate, Btu/hr	All in Btu/hr ft² °F					
										U_o	U_1	U_2	U_3	U_4	U_5
41	3.5	17	24.2	27.2	518	26.7	33.4	34.0	119,600	496	132	452	550	584	585
42	3.5	17	24.1	23.0	520	26.6	33.2	33.9	119,100	496	132	473	547	584	587
43	3.38	17	24.2	27.9	523	26.6	33.3	33.6	118,500	492	127	444	555	591	587
44	3.38	17	24.4	27.0	520	26.6	33.4	33.7	118,800	490	127	448	551	585	583
45	3.38	17	24.5	27.0	521	26.8	33.5	34.0	119,100	489	127	442	551	580	579
46	3.5	17	24.4	26.8	518	27.0	33.7	34.2	118,300	487	129	448	558	586	591
47	3.38	17	24.6	26.6	517	27.0	33.7	34.3	118,200	484	130	449	550	583	577
48	3.38	17	24.8	26.8	515	27.0	33.8	34.4	119,500	484	125	438	545	572	574
49	3.5	17	24.3	23.0	511	27.0	33.4	34.6	118,600	491	130	470	556	580	579
50	3.5	17	24.5	26.5	518	26.9	33.1	34.1	118,200	485	126	444	561	589	583
51	3.38	17	24.8	26.1	513	26.9	33.3	34.2	118,100	478	131	443	552	579	573
52	3.38	17	24.7	26.3	523	26.9	33.6	34.0	117,200	478	123	439	551	579	577
53	3.38	17.2	24.8	25.9	516	26.8	33.5	34.1	118,300	481	123	440	546	575	575
54	3.5	17.2	24.8	25.7	518	26.7	33.4	34.0	119,100	484	122	440	548	576	576
55	3.5	17.1	24.8	25.9	516	26.7	33.4	34.0	119,400	483	117	431	544	575	578
56	3.38	17.1	24.9	25.2	521	26.7	33.4	33.9	118,900	479	116	431	543	575	577
57	3.38	17.1	25.2	27.4	520	26.8	33.3	34.1	120,100	479	116	414	538	570	572
58	3.25	17	25.1	26.1	544	26.8	33.1	33.6	119,600	479	116	424	545	575	575
59	3.25	17	24.8	25.4	540	26.8	33.1	33.7	118,500	479	112	412	544	579	580
60	3.38	17	25.2	25.6	532	26.8	33.1	33.8	118,500	472	121	416	541	576	571
61	3.38	17	25.2	24.1	537	26.9	33.3	33.9	118,700	473	112	424	537	580	570
62	3.38	17.1	25.2	20.7	523	27.0	33.4	34.3	117,100	467	126	449	530	568	572
63	3.25	17.2	25.7	26.3	534	27.0	33.4	33.8	116,400	455	117	396	529	564	564
64	3.13	17.2	25.4	24.8	532	27.0	33.4	33.9	116,600	462	116	412	531	570	571
65	3.13	17	25.5	24.5	536	27.0	33.3	33.8	116,200	459	114	405	527	567	567
66	3.13	17.1	25.5	24.3	534	27.0	33.3	33.7	114,600	452	113	406	523	566	563
67	3.0	17	25.0	24.5	532	27.0	33.3	33.8	115,200	463	125	436	527	566	574

Summary

The main conclusions derived from Experiment 2 are that soluble scale does not form at solids levels well below the saturation solids value and that the liquor used in this experiment (and subsequent ones) is not prone to other types of scale (at least not at lower solids levels).

Experiment 3

Description of Run

This experiment was designed to obtain data on soluble scale formation with a softwood liquor and to relate the scaling behavior to the solubility of Na_2CO_3 and Na_2SO_4 in the liquor. The run was a sequel to Experiment 2, and operating conditions were chosen which were similar to those encountered in the first effect of the mill's evaporator. These are summarized below:

Pressure in vapor head:	12.25 psig	Flow rate:	0.6-0.7 gal/min
Steam pressure:	35 psig	Inlet solids:	33.7-42%
Overall ΔT:	25°F	Discharge solids:	45-50%
Subcooling ΔT:	21°F	Solids by heat balance:	47-52%

There was one significant difference in operating procedure in this experiment compared to Experiment 1. The steam temperature was held fixed and the heat transfer rate allowed to fall as the evaporator scaled. This is in direct contrast to the procedure used in Experiment 1 in which the steam pressure was raised to maintain a constant heat transfer rate as the evaporator scaled.

The evaporator was evaporated in a once-through manner for the first 25 hours. The feed concentration remained at about 34% solids and the discharge solids at about 45% during this period. Fresh liquor was continuously supplied to the evaporator. Neither the concentrated liquor nor the condensate was returned to the feed tank during this period. After 25 hours the system was switched

to the concentrating mode to increase the feed solids level. In this mode concentrated liquor, but not condensed vapor, is returned to the feed tank. After 29 hours, the system was switched to the full recirculation mode, with both concentrated liquor and condensate returned to the feed tank to maintain a constant feed solids level. After 32 hours, the system was again switched to the concentrating mode and continued that way to the end of the run.

Data

Data on evaporator operating conditions and thermal performance are tabulated in Table XVIII. Data on the amount of scale formed, scale distribution and scale composition are given in Table XIX.

Heat Transfer Analysis

The overall resistance to heat transfer expressed as the inverse of the overall heat transfer coefficient for the entire tube is shown as a function of time in Fig. 10. It is evident that scaling is relatively mild during the first 25 hours when the evaporator was operated in a once-through mode. There are some indications of an increase in resistance during the first 6 hours and from 15 to 19 hours. These may or may not be due to scale formation. The total increase in resistance is from 0.215 to 0.24 $\times 10^{-2}$ ft^2 hr °F/Btu in the first 25 hours corresponding to a drop in the heat transfer coefficient from 465 to 417 Btu/hr ft^2 °F. The heat transfer resistance increased more rapidly after the concentrating mode of operation had begun. This is not entirely due to scaling, since the overall solids level within the evaporator is increased and the associated higher liquor viscosities would also be expected to decrease the heat transfer coefficient. The most rapid scaling took place during the final 1.5 hours of the run. If the overall heat transfer resistance is used as a measure of the amount of scale present, it is seen that almost 2/3 of the scale is formed in the last 1.5 hours.

TABLE XVIII

EVAPORATOR OPERATING CONDITIONS AND PERFORMANCE DATA FOR EXPERIMENT 3

Time, hr	Pressure in Vapor Head, psig	Steam Pressure, psig	Overall ΔT, °F	ΔT_{sc}, °F	Flow, lb/hr	Inlet Solids, %	Discharge Solids, %	Solids by Heat Balance, %	Heating Rate, Btu/hr	All in Btu/hr ft² °F					
										U_o	U_1	U_2	U_3	U_4	U_5
1	12.25	35.2	25.4	21.1	416	33.7	45.8	46.5	116,400	461	260	522	520	474	389
2	11.5	35.5	26.1	20.7	366	33.8	47.7	49.1	114,800	442	297	514	480	434	371
3	12.13	35.2	25.2	21.6	391	33.9	45.9	47.7	115,200	459	266	504	496	463	396
4	12.0	35.0	25.4	20.2	366	33.9	46.0	48.4	110,400	437	281	507	498	461	392
5	11.75	35.0	25.5	19.6	379	33.9	45.7	47.5	109,800	433	272	504	453	441	392
6	11.63	35.0	26.5	20.7	394	34.0	45.9	47.4	112,600	426	260	501	455	448	290
7	11.75	35.5	26.2	20.7	396	34.0	45.8	47.0	111,600	428	264	500	454	459	290
8	11.75	35.2	26.6	19.8	411	33.9	45.8	46.6	113,800	429	260	494	450	441	291
9	11.38	35.1	26.5	22.0	367	34.0	46.8	48.6	112,100	424	263	490	437	429	269
10	11.63	35.2	25.9	20.9	361	34.2	46.9	49.3	111,800	434	270	495	442	425	269
11	11.88	35.0	25.4	20.9	370	34.1	46.1	48.2	109,800	435	257	495	459	447	278
12	11.75	35.0	25.9	18.5	377	33.8	45.9	48.0	112,200	435	274	495	451	439	280
13	11.38	35.0	26.4	22.5	389	33.8	46.5	47.3	113,200	432	262	492	446	437	276
14	11.50	35.0	26.1	20.7	378	33.8	46.0	47.9	112,600	434	258	488	443	442	281
15	11.38	35.0	26.2	20.5	393	33.8	46.2	47.2	113,000	433	260	495	453	446	283
16	11.50	35.0	26.4	21.1	374	33.8	45.8	47.9	111,500	425	258	485	442	439	285
17	11.50	35.0	26.4	20.5	395	33.8	45.9	46.9	111,800	426	253	490	447	452	286
18	11.5	35.0	26.5	20.7	394	33.8	45.8	46.9	111,500	422	250	487	447	449	282
19	11.88	35.5	26.5	21.4	376	33.9	45.9	47.8	111,000	420	246	481	442	437	282
20	11.75	35.4	26.6	21.1	382	33.9	46.1	47.5	110,900	418	241	479	437	437	280
21	11.75	35.4	26.6	21.1	370	33.9	46.0	48.0	110,500	417	239	479	440	440	282
22	11.75	35.4	26.5	21.2	406	34.1	45.8	46.5	110,600	419	233	480	445	446	287
23	11.50	35.3	26.7	19.6	400	33.8	45.3	46.6	111,300	418	240	483	443	446	283
24	11.50	35.5	27.0	22.1	382	33.8	45.8	47.3	111,000	413	226	476	445	442	281
25	11.63	35.5	26.5	20.7	393	33.9	45.4	47.1	111,900	423	236	481	450	449	291
26[a]	11.63	35.7	27.1	20.5	410	34.3	45.2	46.9	111,900	415	223	474	456	452	284
27[a]	11.75	35.4	26.4	23.2	391	35.2	46.2	47.8	106,000	404	204	464	453	447	284
28[a]	11.75	35.5	26.5	20.9	397	35.7	46.6	48.3	105,500	399	212	463	438	431	271
29[a]	11.75	35.2	25.9	21.1	409	36.4	46.6	48.0	101,600	394	197	458	435	433	263
30[b]	12.13	35.5	25.3	22.1	371	36.8	47.3	50.0	100,100	398	189	449	433	420	262
31[b]	11.63	35.1	25.0	21.6	370	36.5	46.8	49.1	97,500	392	185	452	435	428	262
32[b]	11.63	35.0	25.2	20.7	375	36.6	46.9	49.1	97,600	389	188	452	433	424	265
33[a]	11.5	35.0	25.6	21.2	391	37.1	47.2	49.1	98,300	385	179	449	428	414	259
34[a]	11.63	35.0	25.0	20.9	396	38.3	47.6	49.6	92,700	372	160	441	436	403	256
35[a]	11.75	35.0	24.8	22.3	390	39.2	48.3	50.4	89,900	364	149	439	431	384	244
36[a]	11.88	35.0	23.9	23.0	387	40.1	48.6	50.6	84,000	353	134	413	436	371	234
36.5[a]	11.75	35.2	24.2	20.9	373	40.8	48.8	52.1	83,600	347	148	431	425	350	203
37[a]	11.63	35.5	25.0	23.8	399	41.2	49.4	51.2	82,100	330	135	406	427	321	177
37.5[a]	11.75	40.5	30.2	23.9	344	41.4	50.5	53.7	82,200	273	172	410	358	166	115
38[a]	11.75	40.7	31.2	25.4	366	42.2	50.0	52.3	75,200	242	155	406	316	111	82

[a] System operating in a concentrating mode.
[b] System operating in a full recirculation mode.

This would amount to a deposition rate of 1.2 lb/hr during this final phase of the experiment.

TABLE XIX

SCALE DISTRIBUTION AND COMPOSITION IN EXPERIMENT 3

Segment 5	704 g
Segment 4	428 g
Segment 3	59 g
Segment 2	19 g
Segment 1	14 g
Total	1224 g

Carbonate as Na_2CO_3	39.9%
Sulfate as Na_2SO_4	53.5%
Calcium	0.44%
Aluminum	0.013%
Chromium	0.016%
Iron	0.097%
Magnesium	0.022%
Silica (as SiO_2)	0.056%

The interpretation of changes in the overall heat transfer coefficient is facilitated by examination of the behavior of the segment coefficients. Plots of relevant segment heat transfer resistances vs. time are given in Fig. 11. The extremely rapid increase in heat transfer resistance when "critical" conditions are reached near the end of the run are clearly evident. With the exception of Segments 1 and 5, the segment resistances change very little until the last stages of the run.

a System operating in a concentrating mode.
System operating in a full recirculation mode.

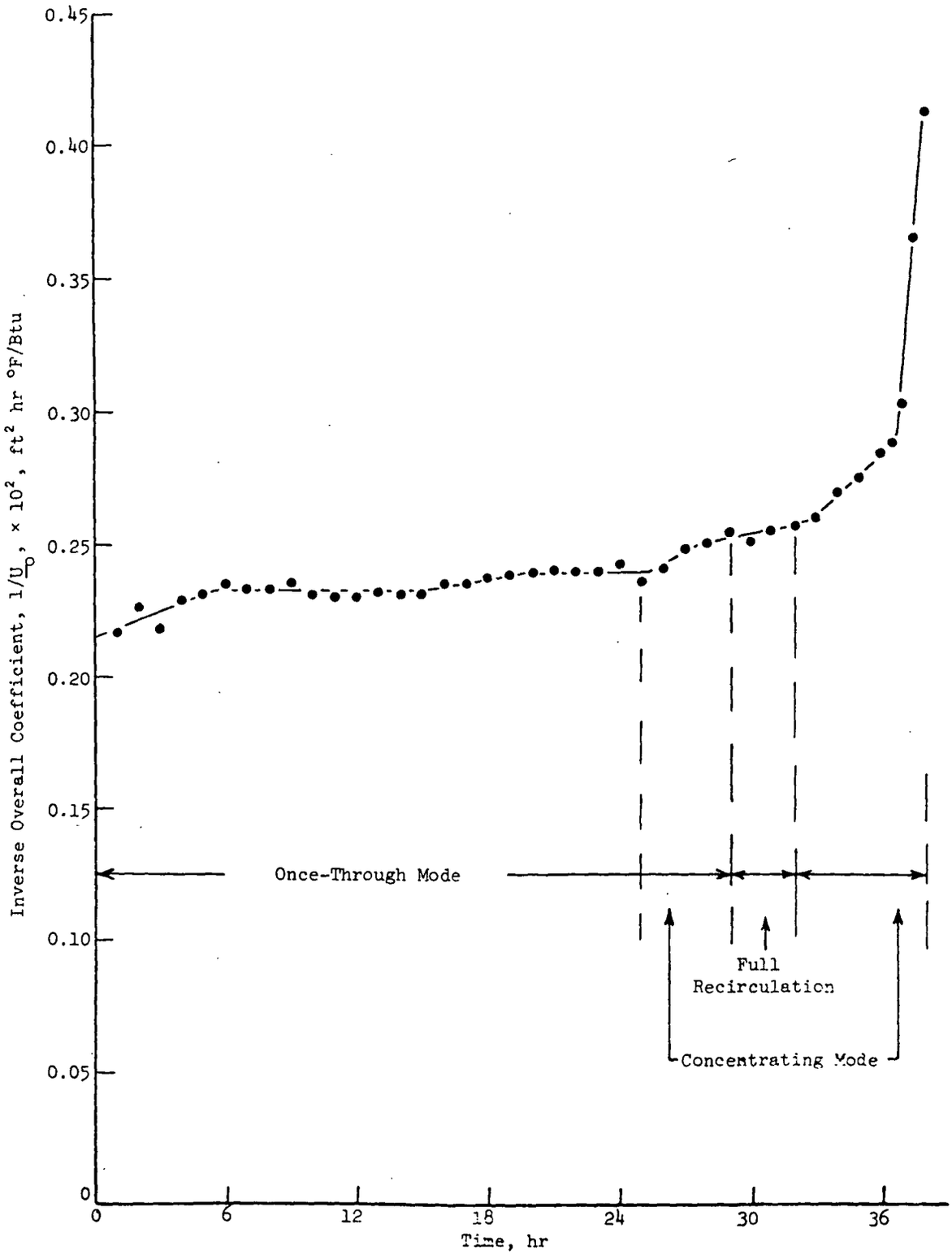

Figure 10. Overall Heat Transfer Resistance in Experiment 3

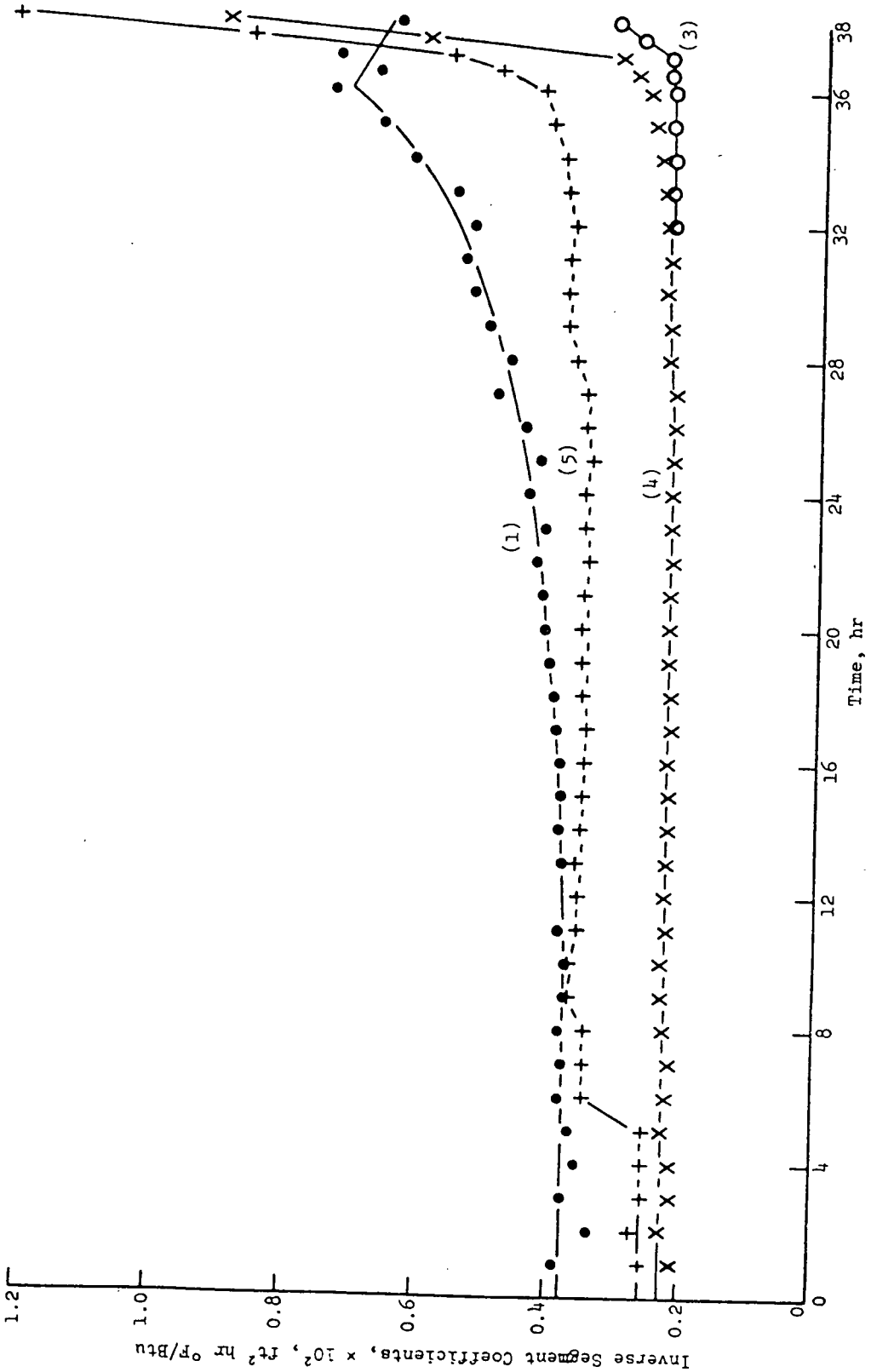

Figure 11. Inverse Segment Coefficients in Experiment 3

It is very unlikely that the resistance increase in the first (bottom) segment is due to scaling. The total amount of deposit found in this segment was only 14 grams, most of which is probably dried liquor solids from the thin film of liquor which remains on the tube surface when the evaporator is drained. The gradual increase in the resistance of the first segment appears to begin about 12 hr after the start of the run, while once-through operation is being maintained. There is a definite increase in Segment 1 resistance before switching to the concentrating mode and increasing the solids feed to the evaporator. The exact reasons for this behavior are not known. The resistance does increase more rapidly after operation was switched to the concentrating mode. This is most likely due to the increased viscosity associated with the higher feed solids.

There are a number of discontinuous increases in the Segment 5 resistance as well as the rapid rise near the end of the run. These may be indicative of "bursts" of scale forming in the time interval between data taken. They could also be caused by partially plugged orifices or "sticking" manometers resulting in an erroneous value of the heat transfer rate in this segment.

It appears that the increase in the overall resistance in the first six hours is due to a significant increase in resistance in the top segment. This would be due to scaling. The increase in the overall resistance during the period from 15 hours until the start of the concentrating mode of operation seems to be definitely associated with the increased resistance in Segment 1, and so is not due to carbonate-sulfate scaling. After the concentrating mode is initiated, the main factor responsible for increasing overall resistances is scaling, although the higher viscosity in the bottom segment also plays a role.

It is of interest to compare these data on scale formation with data on local solids contents of the liquor. Data showing the liquor solids content at different locations along the evaporator tube as a function of time are given in Table XX. The value for $\underline{S}_{\underline{in}}$ is the experimentally measured value for the feed solids. The value for $\underline{S}_5$ (the solids content of the liquor leaving the evaporator tube) was taken to be the measured discharge solids plus a correction for condensation in the vapor head. The correction was plus 1.6% for the first 30 hours and plus 2.2% after 30 hours. Values for the solids contents $\underline{S}_1 \rightarrow \underline{S}_4$ leaving each of the evaporator segments were calculated from the measured heat transfer distributions as discussed previously.

Potential Scale

The degree of saturation reached (and the potential scaling rate) is dependent on both the local solids content and the composition of the black liquor. Data showing the composition of the liquor at various times during the run are given in Table XXI. The data on carbonate, sulfate and total sodium are expressed as wt.% of the compound on the solids. Values of the saturation solids content are taken from the general correlation given in Fig. 1 and 2. Direct measurements of solubility limits were also made which suggest that the actual saturation concentrations (carbonate + sulfate to water ratios) with this liquor were only 85-90% of those predicted by the curves. However, material balances over these solubility determinations did not close very well so the data are somewhat suspect. The values for saturation solids given in Table XXI are believed to be at least as reliable and represent an upper bound to the critical solids for this liquor.

TABLE XX

SOLIDS PROFILE IN EXPERIMENT 3

(All values as wt.% liquor solids)

Time, hr	S_{in}	S_1	S_2	S_3	S_4	S_5
1	33.7	34.6	37.3	40.7	44.2	47.4
2	33.8	35.0	38.3	41.8	45.6	49.3
3	33.9	34.8	37.5	40.7	44.1	47.5
4	33.9	34.8	37.7	40.8	44.2	47.6
5	33.9	34.9	37.7	40.7	44.0	47.3
6	34.0	34.9	37.9	41.2	44.8	47.5
7	34.0	34.9	37.9	41.1	44.8	47.4
8	33.9	34.9	37.9	41.1	44.7	47.4
9	34.0	35.1	38.3	41.7	45.6	48.4
10	34.2	35.3	38.6	42.0	45.8	48.5
11	34.1	35.1	38.1	41.3	45.1	47.7
12	33.8	34.9	37.9	41.1	44.8	47.5
13	33.8	34.9	38.0	41.4	45.3	48.1
14	33.8	34.8	37.8	41.1	44.9	47.6
15	33.8	34.7	37.9	41.2	45.1	47.8
16	33.8	34.8	37.8	40.9	44.6	47.4
17	33.8	34.7	37.8	41.0	44.8	47.5
18	33.8	34.7	37.7	41.0	44.7	47.4
19	33.9	34.8	37.8	41.0	44.8	47.5
20	33.9	34.8	37.9	41.1	45.0	47.7
21	33.9	34.8	37.8	41.1	44.9	47.6
22	34.1	34.9	37.9	41.1	44.7	47.4
23	33.8	34.6	37.6	40.7	44.2	46.9
24	33.8	34.6	37.6	40.9	44.7	47.4
25	33.9	34.7	37.6	40.7	44.3	47.0
26	34.3	35.0	37.7	40.7	44.2	46.8
27	35.2	35.8	38.6	41.7	45.2	47.8
28	35.7	36.4	39.2	42.2	45.7	48.2
29	36.4	36.9	39.7	42.6	46.0	48.2
30	36.8	37.4	40.3	43.1	46.5	48.9
31	36.5	37.1	39.9	43.0	46.6	49.0
32	36.6	37.2	40.0	43.1	46.6	49.1
33	37.1	37.6	40.5	43.6	47.0	49.4
34	38.3	38.7	41.4	44.4	47.6	49.8
35	39.2	39.5	42.2	45.3	48.4	50.5
36	40.1	40.3	42.9	45.9	48.8	50.8
36.5	40.8	41.2	43.7	46.7	49.3	51.0
37	41.2	41.4	44.1	47.3	49.9	51.6
37.5	41.4	42.1	45.8	49.5	51.3	52.7
38	42.2	42.8	46.6	49.9	51.2	52.2

TABLE XXI

COMPOSITION OF FEED LIQUOR DURING EXPERIMENT 3

Time, hr	Solids, %	Na_2CO_3, %	Na_2SO_4, %	Total Sodium, %	Saturation Solids, %
3	33.9	12.5	7.3	20.4	46.7
15	33.8	12.0	7.4	20.8	46.3
34	38.3	11.2	7.6	20.7	46.5
36.5	40.8	11.4	7.2	20.4	47.1
37.5	41.4	11.9	7.0	20.0	47.6
37.5[a]	50.5	10.8	6.0	19.4	49.2

[a]Sample of discharge liquor.

Values of the potential scale at the ends of each segment are given in Table XXII as a function of time. These are based on a constant saturation solids content of 46.7%. It is seen that supersaturated conditions exist in the fifth (top) segment throughout the run. There is a high value of potential scale indicated at 2 hr and this could be associated with scale growth in the top segment during the first part of the run. It should be noted, however, that there is no indication of an increase in potential scale between 5 and 6 hours when a marked drop in the segment coefficient for the 5th segment occurred. In general, the potential scale is fairly mild during the first 30 hours of the run, and there is relatively little scaling indicated during this period. The state of the evaporator during this time period could be characterized as approaching or slightly exceeding saturation at the top of the tube. Under these conditions, sulfate-carbonate scale forms only very slowly and there is little degradation in evaporator performance.

TABLE XXII

POTENTIAL SCALE DURING EXPERIMENT 3

(All values of potential scale in lb/hr)

Time, hr	PS1	PS2	PS3	PS4	PS5
1	-18.2	-13.1	-7.7	-2.95	0.77
2	-15.4	-10.1	-5.39	-1.11	2.42
3	-16.8	-12.1	-7.26	-2.90	0.83
4	-15.8	-11.0	-6.67	-2.61	0.87
5	-16.1	-11.4	-7.04	-2.93	0.60
6	-16.8	-11.6	-6.65	-2.11	0.84
7	-16.9	-11.6	-6.82	-2.12	0.74
8	-17.5	-12.0	-7.05	-2.32	0.76
9	-15.3	-10.2	-5.56	-1.12	1.63
10	-14.8	-9.63	-5.14	-0.90	1.70
11	-15.5	-10.6	-6.13	-1.67	0.98
12	-16.0	-11.0	-6.45	-2.01	0.79
13	-16.5	-11.2	-6.26	-1.51	1.42
14	-16.2	-11.2	-6.47	-1.91	0.90
15	-16.4	-11.0	-6.43	-1.69	1.09
16	-16.1	-11.1	-6.66	-2.21	0.69
17	-17.2	-11.7	-6.90	-2.11	0.83
18	-17.1	-11.8	-6.88	-2.22	0.73
19	-16.2	-11.2	-6.59	-2.01	0.80
20	-16.5	-11.2	-6.56	-1.82	1.01
21	-15.9	-11.0	-6.35	-1.87	0.88
22	-18.0	-11.9	-7.01	-2.30	0.76
23	-17.6	-12.2	-7.41	-2.84	0.21
24	-16.8	-11.6	-6.80	-2.15	0.71
25	-17.1	-12.0	-7.30	-2.68	0.31
26	-17.5	-12.5	-7.70	-2.96	0.11
27	-15.6	-10.7	-6.13	-1.70	1.17
28	-14.9	-10.1	-5.62	-1.15	1.64
29	-14.7	-9.76	-5.33	-0.84	1.72
30	-12.6	-8.06	-4.24	-0.22	2.28
31	-13.0	-8.56	-4.32	-0.11	2.35
32	-13.0	-8.55	-4.26	-0.11	2.49
33	-13.0	-8.26	-3.84	0.34	2.94
34	-11.7	-7.22	-2.92	1.06	3.51
35	-10.4	-6.06	-1.76	1.99	4.27
36	-9.16	-5.11	-1.01	2.48	4.65
36.5	-7.55	-3.88	0.0	2.98	4.76
37	-7.82	-3.60	0.77	3.91	5.80
37.5	-5.78	-1.04	2.99	4.74	6.02
38	-4.82	-0.12	3.39	4.65	5.57

Much higher values of potential scale are obtained when the inlet solids approaches and exceeds 40%. Positive values of potential scale are reached in Segments 3, 4, and 5, and all of these were found to have significant amounts of scale. In addition, the amount of scale found does relate to the duration and magnitude of positive potential scale values. Thus, these data support the concept that sulfate-carbonate scales form because of precipitation from a supersaturated solution, and that bulk solubility considerations (rather than local concentrations at the hot surface) are the controlling factor.

It is of interest to note that the phenomenon of extremely rapid scale growth, found in Experiment 1, did not occur in Experiment 3 even though relatively high values of potential scale were present, until the steam pressure was raised from 35 to 40 psig for the final hour of the run. This is due to the difference in operating procedures in these two runs. In this experinent (3), the steam pressure (hence, thermal driving force) was held constant and the heat transfer rate allowed to decrease as scaling proceeded. Under these conditions, less heat is transferred where scales are present, less concentration then occurs in this zone, and the system tends to become self-limiting as far as scale growth is concerned. In Experiment 1, the driving force was increased to maintain heat transfer rates constant as scaling proceeded. In this mode of operation, there is no self-limiting tendency.

It appears as if two factors are needed to get rapid scale growth. First, the critical solids content must be exceeded by some minimum amount. Second, significant concentration of the liquor must be occurring while in this supersaturated region. It should be noted that the potential scale value itself is dependent only on local state of the liquor (composition and solids content)

and not on heating rates. The data in Experiments 1 and 3 suggest that a combination of high potential scale and high heating rates leads to very rapid scaling.

The difference in behavior between Experiment 3 and Experiment 1 suggests that evaporator operating procedures and control methods can affect the seriousness of soluble carbonate-sulfate scaling problems. It appears to be very undesirable to force an evaporator to maintain a given exit solids content by increasing steam pressure if the target solids is above the critical solids content. It would seem to be much more desirable to allow the solids content to fall so as to accommodate itself to the scale growth.

Summary

This experiment reinforced the conclusions drawn from Experiment 1. Soluble Na_2CO_3-Na_2SO_4 scales can and will form during evaporation of black liquor when the solubility limits of Na_2CO_3 and Na_2SO_4 in the bulk liquor are exceeded. There is a critical solids content for scale formation which is closely linked to the saturation concentration for the liquor. Bulk liquor conditions rather than wall conditions are controlling. Scales can form very rapidly if the saturation solids content is exceeded by a few percent, particularly if a high heat transfer rate is maintained in the supersaturated region. The results seem to indicate that it is undesirable to try to force an LTV evaporator to maintain a discharge solids in excess of the critical solids content of the liquor.

Experiment 4

The main purpose of this experiment was to see if the addition of caustic to the liquor so as to give a liquor with a very high residual active alkali could prevent, or significantly delay the onset of soluble carbonate-sulfate scale formation. The liquor used in Experiment 4 was a fresh 450-gallon

portion of liquor from Experiment 2. (This is the softwood liquor concentrated to about 34% solids.) To this was added 75 lb of NaOH (as a 34% solution). This raised the residual active alkali content of the liquor to 8.3% on the solids (as Na_2O). This is equivalent to a RAA content of 14.3 gpl as Na_2O in a 16% solids liquor.

Description of Run

The experiment was carried out in two distinct stages, the first with operating conditions similar to those used in Experiment 3 and the second at a much higher total flow rate. The system was operated in the concentrating mode from the beginning of the run so as to increase the feed solids content and generally raise the solids level in the evaporator. After eight hours of operation which brought the discharge solids level over the critical solids level, the system was switched to the full recirculation mode to maintain a constant feed solids level. This was continued for another two hours which served to complete the first part of the run. At this time the flow rate of liquor through the system was increased by about a factor of three. The magnitude of this change was great enough to cause some problems in running the system and it took about three hours to stabilize operation. Additional changes in operating variables were made over the next three hours so it was not until 16 hours after startup before the final operating conditions were attained. The system was switched back to the concentrating mode at the beginning of the high flow rate portion of the run. This was maintained until 19.5 hours after start-up, when the system was again switched to a full recirculation mode for the remainder of the run.

Data

Data on operating conditions and thermal performance during Experiment 4 are given in Table XXIII. Data on liquor and scale composition and the total amount of scale found are given in Table XXIV. The distribution of the weight of the deposit along the tube was not determined in this experiment. The saturation solids contents in Table XXIV were determined from the general curves in Fig. 1 and 2. The calculated solids profile along the evaporator tube during this experiments is summarized in Table XXV. The value for the solids content leaving the 5th segment, S_5, is taken to be the measured discharge solids plus 1.1% for the first part of the run, and as just the measured discharge solids during the high flow rate part of the run.

Analysis of First Part of Run

Examination of the heat transfer data during the first part of the run shows that the evaporator was scaling right from the beginning. There is a steady decline in the overall heat transfer coefficient from an initial value of 446 to 317 Btu/hr ft^2 °F in only ten hours. More importantly, there is a parallel decline in the heat transfer coefficients for Segments 4 and 5 (the top two) so that scale formation is definitely indicated. Heat transfer resistances (inverse coefficients) for Segments 3, 4 and 5 are plotted vs. time in Fig. 12 for the low velocity portion of this experiment. The steady increase in resistance for Segments 4 and 5 is evident, while Segment 3 shows no indication of scaling. It is noteworthy that the solids content in Segment 3 is always less than the saturation solids content of 45.7% (average of the values in Table XXIV) for this liquor, while this value is exceeded in Segments 4 and 5. Clearly the addition of caustic to the liquor did not prevent soluble carbonate-sulfate scale formation. In fact, the addition of NaOH lowered the saturation solids content

TABLE XXIII

EVAPORATOR OPERATING CONDITIONS AND PERFORMANCE DATA FOR EXPERIMENT 4

Time, hr	Pressure in Vapor Head, psig	Steam Pressure, psig	Overall ΔT, °F	ΔT_{sc}, °F	Flow, lb/hr	Inlet Solids, %	Discharge Solids, %	Solids by Heat Balance, %	Heating Rate, Btu/hr	All as Btu/hr ft^2 °F					
										U_o	U_1	U_2	U_3	U_4	U_5
1[a]	12.0	35.0	23.2	21.1	405	34.5	45.4	45.9	103,000	446	254	456	445	447	317
2[a]	11.63	35.2	23.6	23.0	378	35.4	46.1	47.9	101,400	432	244	441	431	424	297
3[a]	11.88	35.1	22.7	22.5	391	36.0	46.2	47.2	95,800	424	232	436	436	427	274
4[a]	11.75	35.2	23.0	23.0	391	36.9	46.7	48.1	94,400	412	225	433	428	405	264
5[a]	12.0	36.0	22.9	23.0	372	37.5	46.8	49.1	91,300	400	219	419	423	371	231
6[a]	12.25	35.1	22.3	23.4	398	38.3	47.0	47.9	84,200	379	195	416	444	370	222
7[a]	11.75	35.1	23.0	22.1	389	38.9	47.4	48.8	82,400	359	202	416	435	327	189
8[a]	12.0	35.0	22.3	24.8	401	39.6	47.1	48.2	76,800	346	153	394	434	305	177
8.5[b]	11.88	35.1	22.3	23.4	398	39.7	47.2	48.0	73,200	330	162	398	441	303	169
9[b]	12.0	35.3	22.4	23.0	398	39.6	47.2	47.9	73,200	328	150	393	438	297	168
9.5[b]	11.38	35.0	22.3	20.9	370	39.9	47.5	49.1	72,700	327	178	407	429	281	160
10[b]	11.75	35.0	22.7	23.6	388	39.9	47.1	48.2	71,600	317	147	392	437	279	153
13[a]	12.0	35.0	25.0	17.8	1074	40.7	42.5	42.2	51,900	208	86	101	205	402	213
14[a]	12.0	35.0	25.0	17.5	1094	41.3	43.3	42.8	53,300	214	89	101	195	396	223
15[a]	12.12	40.0	29.9	19.8	1091	41.6	43.9	43.8	71,400	240	83	112	257	424	215
16[a]	11.75	44.0	34.0	21.2	1076	42.6	45.8	45.7	88,600	262	89	150	331	411	202
17[a]	11.5	44.0	34.4	19.6	1057	43.8	46.3	47.0	85,200	249	85	155	326	387	180
18[a]	11.62	44.2	34.0	20.9	1093	44.2	46.8	46.8	78,000	231	89	141	316	348	181
19[a]	11.75	44.2	33.6	20.7	1103	44.9	47.2	47.2	70,200	210	85	123	299	313	164
20[b]	11.75	44.0	33.7	20.9	1140	45.3	47.5	47.2	64,000	192	81	116	264	270	147
21[b]	11.87	44.2	32.9	20.7	1111	45.5	47.6	47.4	61,500	188	87	122	271	256	138
21.5[b]	12.0	43.0	30.1	9.7	1109	45.6	48.4	48.5	71,700	239	179	336	314	190	113
22[b]	11.13	44.2	34.6	8.8	1105	45.8	48.4	48.5	66,800	194	223	337	194	110	85
22.5[b]	11.5	44.0	33.0	10.3	1129	45.9	48.1	48.2	60,600	184	200	293	164	109	84

[a] System operating in concentrating mode.
[b] System operating in full recirculation mode.

(because of the increased concentration of the sodium common-ion in the liquor) and the evaporator scaled at a slightly lower solids content.

TABLE XXIV

LIQUOR AND SCALE COMPOSITION IN EXPERIMENT 4

Time, hr	Solids, %	Na_2CO_3, %	Na_2SO_4, %	RAA (as Na_2O), %	Total Sodium, %	Saturation Solids Content, %
6	38.3	11.3	7.1	8.3	21.0	46.5
7	38.9	10.9	7.2	8.5	21.7	45.6
8.5	39.7	11.1	7.3	8.4	21.8	45.7
18	44.2	11.15	7.3	8.2	22.3	44.9
21	45.5	10.9	7.2	8.2	21.3	46.1
22.5[a]	48.1	11.2	7.2	8.0	22.1	45.2

Scale Composition

Na_2CO_3	39.5%
Na_2SO_4	53.0%
Calcium	0.36%

Total amount of scale formed: 1592 g

[a]Sample of discharge liquor; all others inlet liquors.

Analysis of High Velocity Part of Run

The heat transfer data are more complicated to interpret in the high velocity part of the run because the heat transfer distribution along the tube is changed markedly. A much greater fraction of the evaporator is used to supply the sensible heat load. From 13 hours to 21 hours (until the subcooling was cut to about 10°F) the first two segments were used solely to supply sensible heat, and they are characterized by very low heat transfer coefficients. The coefficient

TABLE XXV

SOLIDS PROFILE DURING EXPERIMENT 4

(All as wt.%)

Time, hr	S_{in}	S_1	S_2	S_3	S_4	S_5
1	34.5	35.3	38.0	40.8	44.0	46.5
2	35.4	36.2	38.8	41.7	44.8	47.2
3	36.0	36.8	39.3	42.2	45.2	47.3
4	36.9	37.7	40.1	42.9	45.8	47.8
5	37.5	38.2	40.7	43.4	45.9	47.9
6	38.3	38.8	41.2	44.0	46.6	48.1
7	38.9	39.5	42.0	44.9	47.1	48.5
8	39.6	39.8	42.1	44.9	46.9	48.2
8.5	39.7	40.0	42.3	45.0	47.1	48.3
9	39.6	39.9	42.2	44.9	47.0	48.3
9.5	39.9	40.4	42.7	45.5	47.5	48.6
10	39.9	40.1	42.4	45.2	47.1	48.2
13	40.7	40.7	40.7	40.9	41.9	42.5
14	41.3	41.3	41.3	41.6	42.6	43.3
15	41.6	41.6	41.6	42.1	43.3	43.9
16	42.6	42.6	42.6	43.6	45.1	45.8
17	43.8	43.8	43.9	44.7	45.8	46.3
18	44.2	44.2	44.2	45.1	46.2	46.8
19	44.9	44.9	44.9	45.7	46.6	47.2
20	45.3	45.3	45.3	46.0	46.9	47.5
21	45.5	45.5	45.5	46.2	47.0	47.6
21.5	45.6	45.7	46.6	47.4	48.0	48.4
22	45.8	46.1	47.1	47.7	48.1	48.4
22.5	45.9	46.0	47.0	47.4	47.8	48.1

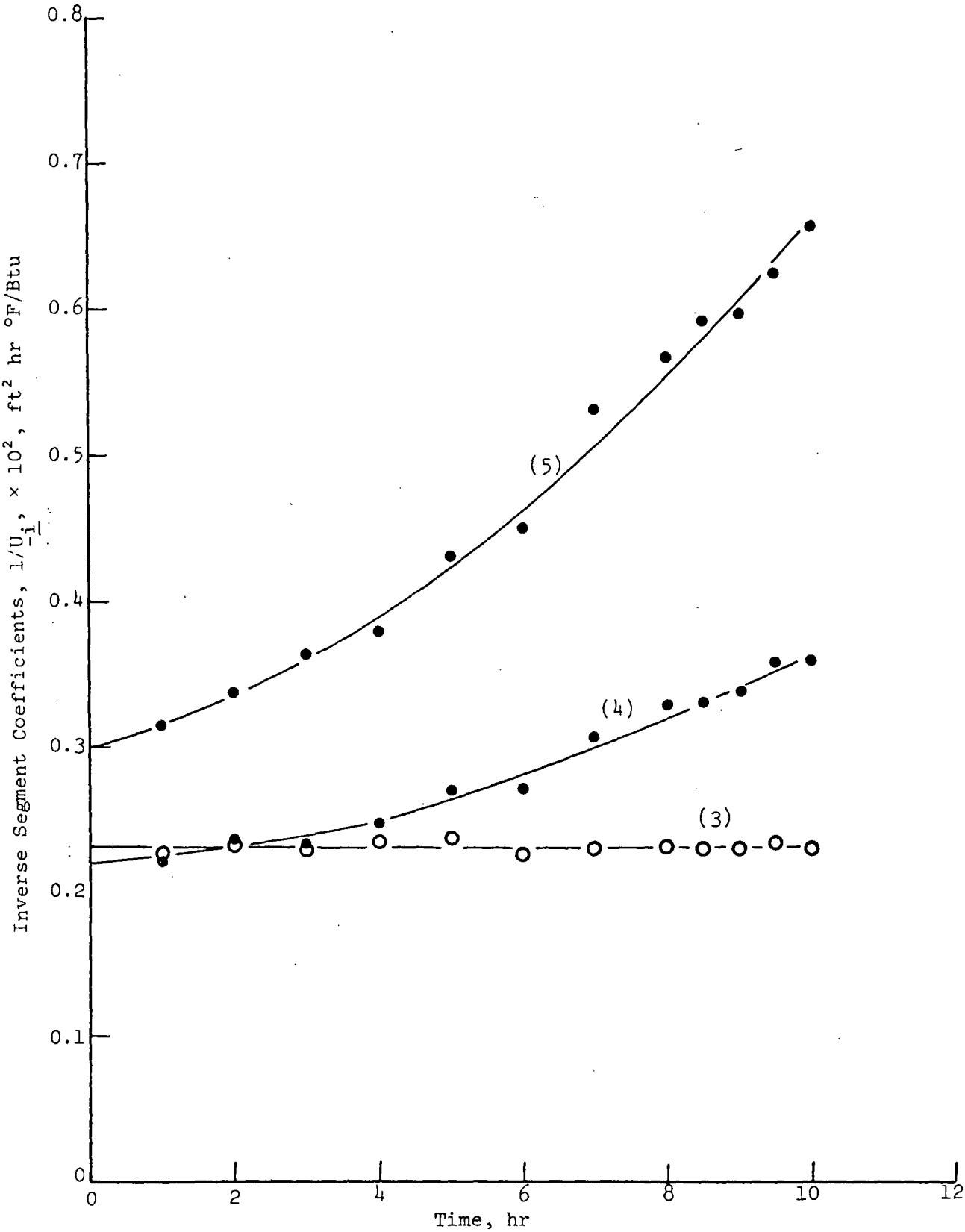

Figure 12. Inverse Segment Coefficients for the Low Velocity Portion of Experiment 4

in the third segment is quite variable since it is so close to the transition zone from subcooled to bulk boiling. The marked drop in the heat transfer coefficient in the third segment during the last hour of the run is due to rapid scale formation. The top two segments (4 and 5) are sufficiently far removed from the transition zone so that the decline in heat transfer coefficient is indicative of scale growth. Heat transfer resistances (inverse coefficients) for these latter two segments are plotted vs. time in Fig. 13 for this high velocity part of the run. The onset of scaling is rather clearly defined, with the rate increasing with time and becoming very rapid in the final hour or so of the run.

One characteristic of operation at high velocity is that there is relatively little concentration change along the evaporator. The solids tend to increase only slightly along the tube so that scale growth tends to take place more uniformly along the tube. During the first few hours of operation at high velocity the entire tube is below the saturation solids content of the liquor and one would expect that some of the scale which formed during the low velocity part of the experiment was redissolved. At the end of the run, the feed liquor is approaching the saturation solids content and practically the entire tube is in a scaling region.

The relationship between carbonate-sulfate solubility limits and the scaling rate can be shown by taking the slopes of the curves in Fig. 12 and 13 at various times and plotting them vs. the solids content of the liquor leaving that segment at that time. This is equivalent to plotting $d/dt\ (1/U_i)$, defined previously as the scaling rate based on heat transfer, vs. solids content. Such a plot is shown in Fig. 14. The data break into two distinct groups for the low flow and the high flow part of the run. The higher scaling rates at the same

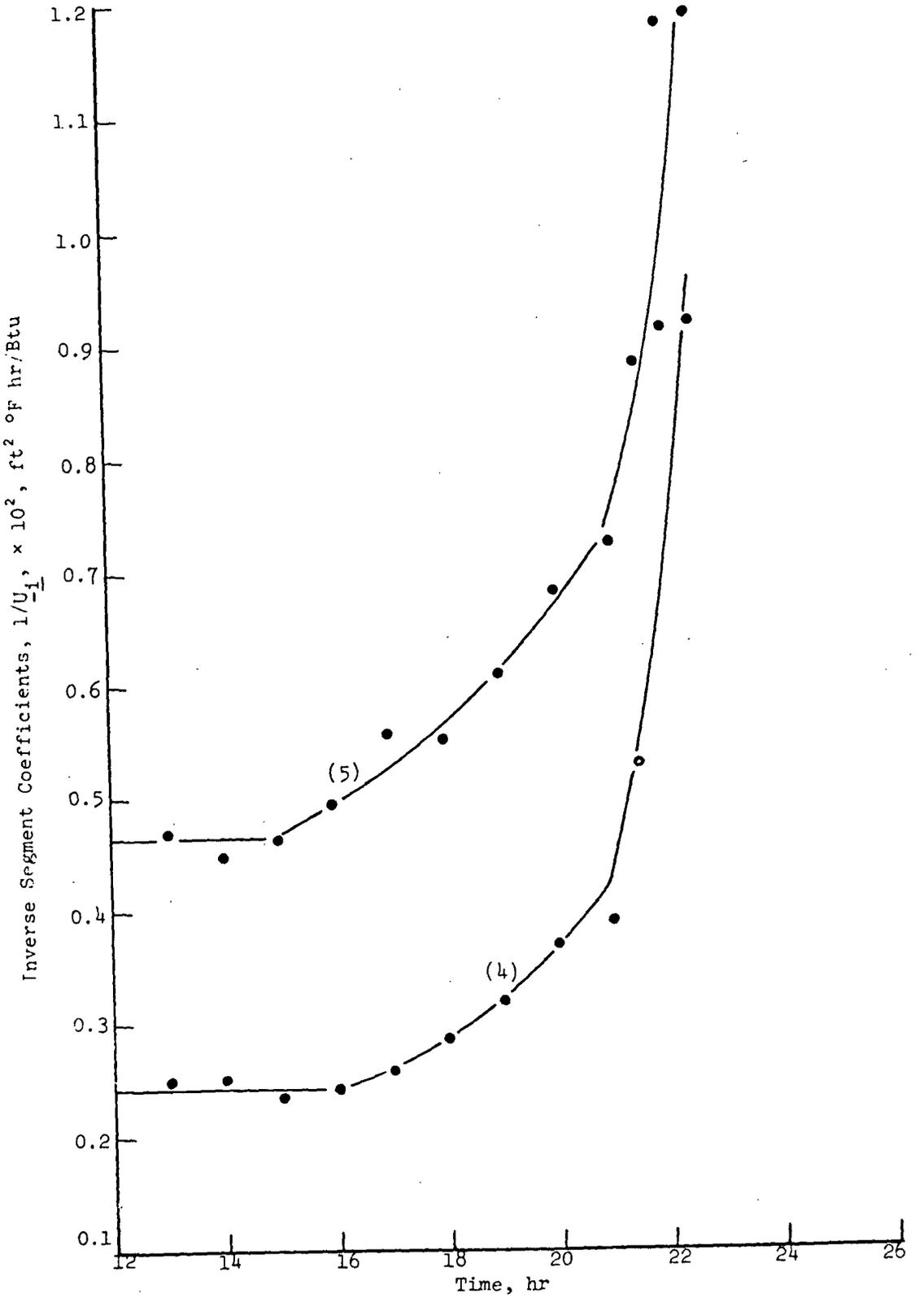

Figure 13. Inverse Segment Coefficients for the High Velocity Portion of Experiment 4

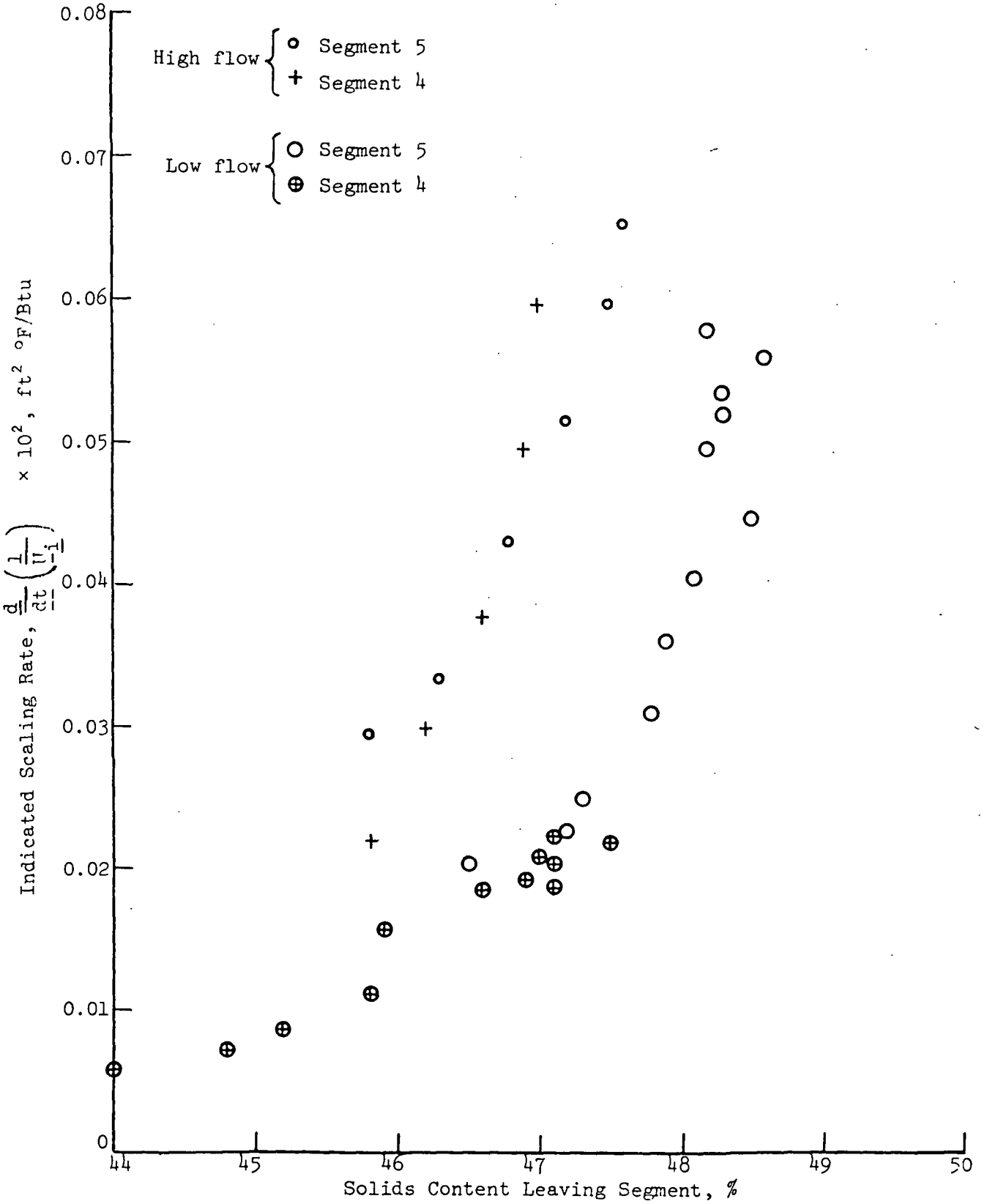

Figure 14. Indicated Scaling Rate Vs. Solids Content in Experiment 4

solids contents for the high flow portion is as would be expected from the potential scale concept, since potential scale is directly proportional to feed rate [see Equation (6)]. These data show a very rapid increase in scaling rate for a small increase in solids content above the critical value. Thus, there is, in fact, a definite operational limit for this kind of an evaporator (a "critical" solids) beyond which rapid scaling sets in. This limit is obviously very closely related to the saturation solids content determined from the solubility curves (45.7% solids in this case).

Summary

The addition of caustic to black liquor to increase the residual active alkali content of the liquor to over 8% on the solids (over 14 gpl in weak liquor) as Na_2O did not have any beneficial effect on preventing or retarding scaling once the critical solids content of the liquor was reached. The effect of caustic addition was exactly as would be predicted from solubility considerations alone; i.e., caustic addition decreases the solubility of Na_2CO_3 and Na_2SO_4 in black liquor. The results of this experiment are in complete agreement with the preceding experiments and lend additional support to the concept of soluble scale growth being governed almost completely by bulk solubility considerations.

Experiment 5

This experiment was concerned with the effect of fiber in the liquor on scale formation. The main objective was to determine if fiber caused scales to form when the bulk liquor concentration was significantly less than the saturation concentration.

Description of Run

The liquor used in this experiment was a fresh portion of the softwood liquor which had been concentrated to about 34% solids in Experiment 2. Three

pounds of an unbleached softwood kraft pulp were added to 450 gallons of liquor. This is equivalent to a fiber content of about 0.2% on the liquor solids, or about 3 lb/1000 gal of weak liquor. The fibers were dispersed in water and added to the liquor in the heated, stirred feed tank. Because of a leaky steam valve on the steam supply to the feed tank, the liquor was heated to 75°C and concentrated in the feed tank to 39.6% solids in the few days before the run was carried out. Thus, the liquor concentration at the start of the run was close to 40% solids.

Operating variables for this run were chosen to approximate those used in Experiment 3 (which was carried out with the same liquor without the fiber added). Steam pressure and head pressure are both slightly lower in Experiment 5 (33.5 and 10 psig vs. 35 and 12 psig) than in Experiment 3. The subcooling was also slightly less (16-18°F compared to 20-22°F). The system was started in the concentrating mode, switched to the recirculating mode after 3 hours and switched back to the concentrating mode at 7 hours. The steam pressure was held constant so that the heat transfer rate decreased as scaling proceeded.

Data

Data on operating conditions and thermal performance for this experiment are given in Table XXVI. The solids profile along the evaporator tube is summarized in Table XXVII. Data on liquor and scale composition and scale distribution are given in Table XXVIII. The presence of the fiber in the liquor caused some problems in liquor analysis. In particular, the values for the total sodium appear to be high. Thus, it appears better to take the value for the saturation solids of 46.7% as indicated in Experiment 3 rather than the average value of 45.5% based on the data in Table XXVIII.

TABLE XXVI

EVAPORATOR OPERATING CONDITIONS AND PERFORMANCE DATA FOR EXPERIMENT 5

Time, hr	Pressure in Vapor Head, psig	Steam Pressure, psig	Overall ΔT, °F	ΔT_{sc}, °F	Flow, lb/hr	Inlet Solids, %	Discharge Solids, %	Solids by Heat Balance, %	Heating Rate, Btu/hr	All as Btu/hr ft² °F					
										U_o	U_1	U_2	U_3	U_4	U_5
1.5[a]	10.25	33.0	26.5	14.6	429	40.5	49.2	49.8	81,700	309	197	431	377	250	142
2.5[a]	10.0	33.5	27.4	17.3	381	41.1	48.9	50.3	71,800	264	185	415	344	188	109
3.5[b]	10.0	33.5	26.8	14.9	431	41.5	49.0	48.7	66,500	249	193	419	323	154	92
4.5[b]	9.88	33.2	26.7	15.7	371	41.6	48.7	49.7	62,600	235	179	408	311	152	70
5.5[b]	9.25	33.2	27.7	16.4	388	41.8	48.9	49.5	62,900	228	180	399	296	126	61
6.5[a]	9.5	33.2	27.2	16.4	397	41.9	48.7	49.1	60,900	225	185	401	294	136	77
7.5[a]	9.75	33.5	27.3	18.2	397	42.2	48.4	49.3	60,800	224	163	390	307	132	74
8.0[a]	9.75	33.5	27.4	18.4	407	42.6	48.8	49.4	59,700	219	161	395	295	131	74
8.5[a]	9.38	33.5	27.7	17.6	407	42.9	49.1	49.7	59,500	216	164	389	280	126	67
9.0[a]	9.88	33.5	27.5	16.9	365	43.1	49.0	50.6	57,100	208	166	380	274	102	68

[a] System operating in concentrating mode.

[b] System operating in recirculating mode.

TABLE XXVII

SOLIDS PROFILE DURING EXPERIMENT 5

(All values as wt.%)

Time	S_{in}	S_1	S_2	S_3	S_4	S_5
1.5	40.5	41.3	44.0	46.8	48.8	49.9
2.5	41.1	41.8	44.5	47.1	48.7	49.6
3.5	41.5	42.3	45.3	47.7	49.0	49.7
4.5	41.6	42.3	45.2	47.6	48.8	49.4
5.5	41.8	42.5	45.4	47.9	49.0	49.6
6.5	41.9	42.6	45.4	47.6	48.8	49.4
7.5	42.2	42.7	45.3	47.4	48.5	49.1
8.0	42.6	43.1	45.7	47.9	48.9	49.5
8.5	42.9	43.4	46.1	48.3	49.3	49.8
9.0	43.1	43.7	46.3	48.4	49.2	49.7

TABLE XXVIII

LIQUOR COMPOSITION AND SCALE COMPOSITION AND DISTRIBUTION IN EXPERIMENT 5

Time, hr	Solids, %	Na_2CO_3, %	Na_2SO_4, %	Total Sodium, %	Saturation Solids Content, %
0.5	39.6	12.2	7.0	22.5	44.7
5.5	41.8	11.9	6.85	21.3	45.9
9.0	43.1	11.6	6.85	21.1	46.3
9.0[a]	49.0	12.0	6.8	22.4	45.0

Scale Composition

Na_2SO_4	50.8%
Na_2CO_3	38.8%
Calcium	0.6%
Fiber	1.4%

Scale Distribution

Segment 1	0 g
Segment 2	31 g
Segment 3	50 g
Segment 4	331 g
Segment 5	948 g
	1360 g

[a]Discharge sample.

Analysis of Data

Because of the high feed solids at the beginning of the run, conditions at the top of the evaporator were beyond the saturation solids content from the start of the run. Scaling began immediately in this experiment. Values of the thermal resistances are plotted vs. time in Fig. 15. It is clear that rapid scaling conditions are indicated for Segments 4 and 5 from the start. There is a good deal of scatter in the high resistance data because the heat transfer rates are very small and the manometer readings (from which the segment heat transfer rates are calculated) are very small. Thus, errors in reading the meniscus or caused by the meniscus sticking on dirt or by air bubbles in the lines are greatly magnified. The indicated high scaling rates for the top two segments are verified by the measured scale distribution.

Relatively little scale was found in the third segment, which suggests that conditions in this segment are just below the critical value. With this particular liquor, it appears that rapid scaling does not set in until solids contents of 48.5% or more are reached.

The experience with this liquor with fiber present may be compared with that in Experiment 3 when the fiber was absent. It appears that rapid scaling set in at about 49.5 to 50% solids in Experiment 3 and at about 48.5 to 49% solids in this run. This difference is relatively small and may not be significant.

In any event, there is no evidence that the presence of fibers causes carbonate-sulfate scales to set in when the bulk liquor solids content is below the saturation solids content of the liquor. Bulk solubility considerations still control the onset and growth of soluble sulfate-carbonate scales. The fiber is definitely incorporated into the scale. The deposit was much rougher

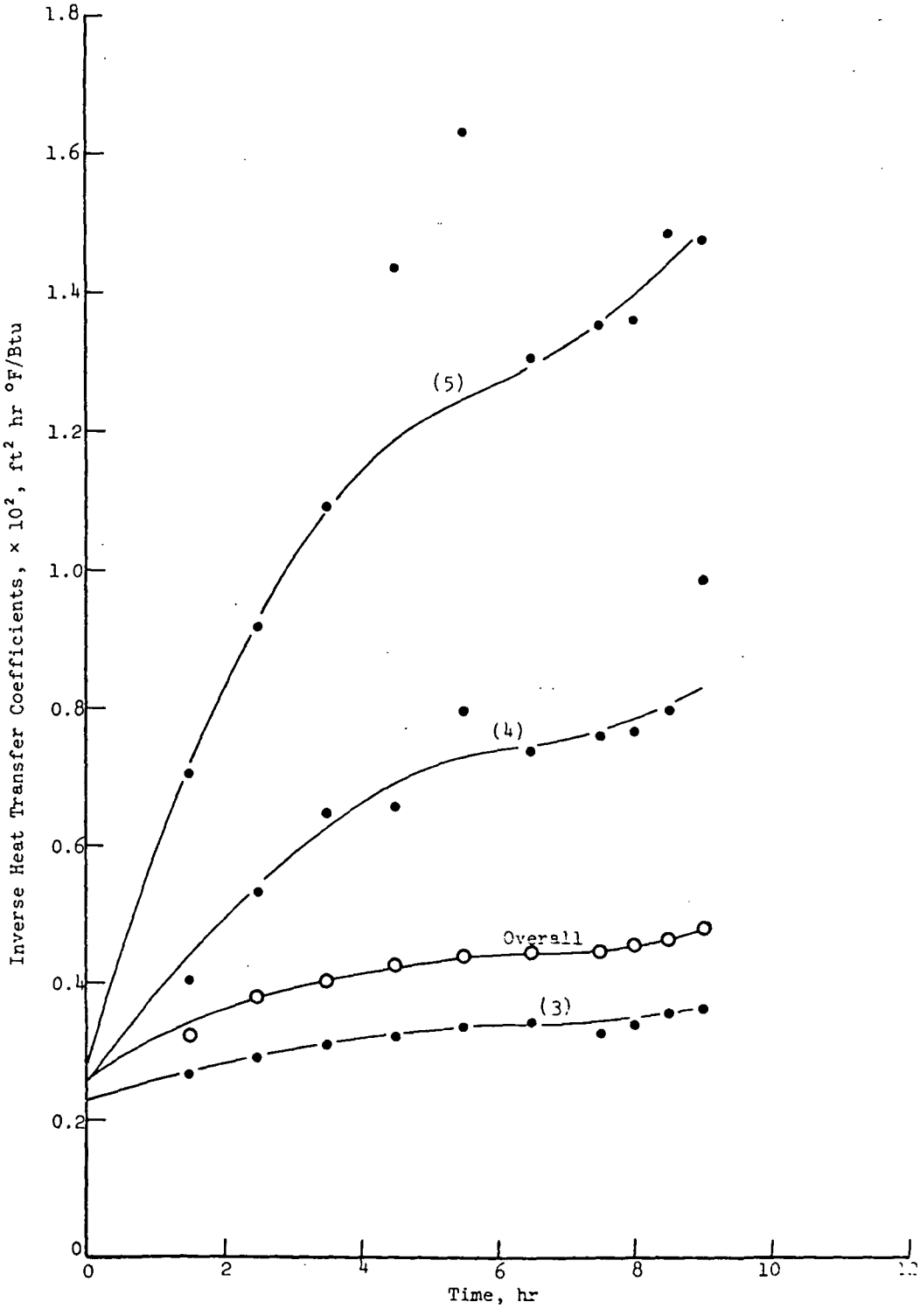

Figure 15. Heat Transfer Resistances in Experiment 5

in appearance than the previous deposits, and many fibers could be seen. Analysis of the scale composition showed fibers to be 7 times higher in the deposit than in the liquor itself. It is very likely that fibers do cause a more rapid scale growth once the critical solids content is exceeded, although that is not unequivocably shown by these results. It is significant that very little or no scale was found in the first three segments. This is clear evidence that the saturation limit can be approached quite closely without scaling, even when fibers are present.

An interesting feature of this run was that the solids content leaving the evaporator tube approached a constant value even though the feed solids increased gradually during the run. This shows the self-limiting nature of the scale growth when the steam temperature is held fixed. As less heat is transferred in a given segment, the rate of scale growth in that segment also decreases. If an attempt is made to increase the heat transfer rate under these circumstances, rapid scaling sets in.

Summary

This experiment showed that the presence of a relatively large amount of fiber in the liquor did not cause scaling to set in at solids contents appreciably below the saturation solids content of the liquor. As in all of the other experiments, the solubility of carbonate and sulfate in the bulk liquor controlled scale growth. The fiber was preferentially incorporated into the scale and did affect scale morphology markedly. There are some indications that the presence of fiber did cause a more rapid scale growth once the critical conditions were exceeded. However, the basic controlling factor is bulk solubility.

Experiment 6

This experiment was carried out to see if scale-free operation could be continued with discharge solids levels well beyond the saturation value simply by maintaining high liquor velocities through the tube. The main objective was to see if evaporator operating variables had any effect on scaling other than their effect on the solids level at various positions along the evaporator tube.

Description of Run

The liquor used in this run was a fresh batch of the softwood liquor concentrated to about 34% solids in Experiment 2. The system was operated in a concentrating mode for the full duration of the run. The feed rate was maintained at about 2 gal/min during the run. This is about 3 times the flow rate used in most of the previous runs and corresponds to an all-liquor velocity of about 12 ft/min. This was about the maximum flow rate which could be handled without a major change in the system. In order to avoid the very poor heat transfer rates in an extended subcooled region such as was found to occur in the high flow rate portion of Experiment 4, the subcooling was held at zero by bringing in the feed liquor at the same temperature as the boiling liquor in the vapor head.

Data

Data on the operating conditions and the thermal performance of the evaporator are summarized in Table XXIX. Data on liquor and scale composition are presented in Table XXX. The solids profile along the tube as a function of time is given in Table XXXI.

TABLE XXIX

EVAPORATOR OPERATING CONDITIONS AND PERFORMANCE DATA FOR EXPERIMENT 6

Time, hr	Pressure in Vapor Head, psig	Steam Pressure, psig	Overall ΔT, °F	ΔT_{sc}, °F	Flow, lb/hr	Inlet Solids, %	Discharge Solids, %	Solids by Heat Balance, %	Heating Rate, Btu/hr	All as Btu/ft² hr °F					
										U_o	U_1	U_2	U_3	U_4	U_5
0.5	7.63	32.0	34.2	16.7	1156	35.2	39.0	39.3	132,000	388	97	235	422	450	433
1.0	9.38	30.0	26.2	1.1	1078	35.9	40.6	41.0	130,200	500	391	554	535	527	563
1.5	8.5	30.0	28.3	2.2	1142	36.4	40.7	40.9	122,000	434	166	500	528	523	527
2.0	8.75	29.8	27.5	1.1	1119	36.9	41.2	41.6	121,700	444	216	530	529	528	540
2.5	8.75	30.0	27.4	1.4	1155	37.5	42.3	42.1	122,900	450	232	534	527	523	538
3.0	9.38	30.0	26.5	-0.2	1129	38.5	42.7	43.5	123,800	470	372	522	513	518	538
3.5	8.38	31.0	27.9	1.8	1134	38.7	43.4	43.6	124,000	447	210	512	504	495	519
4.0	7.88	30.2	28.2	2.7	1161	39.4	43.6	43.9	118,000	421	171	489	512	509	511
4.5	8.88	31.2	26.7	-0.2	1139	40.0	44.9	45.2	123,800	466	331	522	497	505	526
5.0	7.75	30.5	28.3	1.8	1152	41.1	45.5	45.8	115,500	409	196	501	499	492	500
5.5	9.25	30.0	24.2	-1.8	1174	41.4	46.2	46.7	124,900	518	469	541	500	492	517
6.0	7.63	31.0	28.6	1.6	1171	42.5	46.6	47.2	112,700	396	183	476	476	480	460
6.5	7.25	30.0	28.2	1.1	1212	43.4	47.1	48.0	111,400	398	235	481	477	473	443
7.0	8.38	30.0	25.9	-2.7	1227	43.5	48.2	48.2	111,200	431	454	504	460	446	360
7.5	7.25	30.0	27.9	-2.5	1187	44.5	48.7	48.5	91,100	328	356	412	367	307	245
8.0	5.0	30.2	33.7	-1.4	1176	45.1	48.8	48.8	84,700	253	227	353	324	265	204

Concentrating mode used for the entire run.

TABLE XXX

LIQUOR AND SCALE COMPOSITION IN EXPERIMENT 6

Time, hr	Solids, %	Na_2CO_3, %	Na_2SO_4, %	Total Sodium, %	Saturation Solids Content, %
0.5	35.2	11.8	7.0	21.8	45.4
4.0	39.4	11.8	6.9	22.2	45.1
6.0	42.5	12.0	6.8	20.3	47.2
7.5	44.5	11.7	6.8	22.1	45.3
8.0	45.1	12.1	6.8	22.1	45.1
8.0[a]	48.8	11.4	6.8	21.6	45.9

Scale Composition

Na_2CO_3	26.3%
Na_2SO_4	51.3%
Calcium	0.7%

Total weight of scale 266 g

[a]Discharge sample.

Analysis of Data

The overall coefficient is not a very useful measure of scaling in this experiment because it is extremely sensitive to the sensible heat load at any given time. The very strong impact of small changes in inlet subcooling is very evident in examining the heat transfer coefficient for Segment 1. This varies by almost a factor of three for changes in subcooling from about +2°F to -2°F. This change in the coefficient for Segment 1 is a direct reflection of changes in the heat transfer rate in this segment. Heat transfer is very poor in the sensible heat zone and increases rapidly as soon as net boiling occurs.

TABLE XXXI

SOLIDS PROFILE IN EXPERIMENT 6

(All values as wt.%)

Time, hr	S_{in}	S_1	S_2	S_3	S_4	S_5
0.5	35.2	35.2	35.4	36.5	37.9	39.3
1.0	35.9	36.5	37.5	38.5	39.6	40.9
1.5	36.4	36.5	37.5	38.5	39.8	41.0
2.0	36.9	37.2	38.2	39.2	40.3	41.5
2.5	37.5	37.7	38.8	40.1	41.3	42.6
3.0	38.5	39.0	39.9	40.9	41.9	43.0
3.5	38.7	39.0	40.0	41.1	42.4	43.7
4.0	39.4	39.5	40.5	41.5	42.7	43.9
4.5	40.0	40.6	41.7	42.7	43.9	45.2
5.0	41.1	41.3	42.3	43.4	44.6	45.8
5.5	41.4	42.4	43.4	44.4	45.4	46.5
6.0	42.5	42.7	43.6	44.7	45.8	46.9
6.5	43.4	43.7	44.5	45.4	46.4	47.4
7.0	43.5	44.5	45.5	46.6	47.6	48.5
7.5	44.5	45.4	46.5	47.4	48.3	49.0
8.0	45.1	45.5	46.6	47.6	48.5	49.1

The best indicators of scale formation are the coefficients for the top three segments. Values of the thermal resistance for these segments (inverse coefficients) are plotted vs. time in Fig. 16. It is clear that scaling sets in at a rather discrete time for each segment and occurs at a rapid rate thereafter. The run was terminated shortly after the onset of rapid scaling. This is the reason that only a relatively small amount of scale (266 g) was found. The onset of rapid scaling appears to occur when the solids content reaches 47-48%. Although this is slightly higher than the indicated saturation solids content of 45.5%, it is comparable to the solids range in which rapid

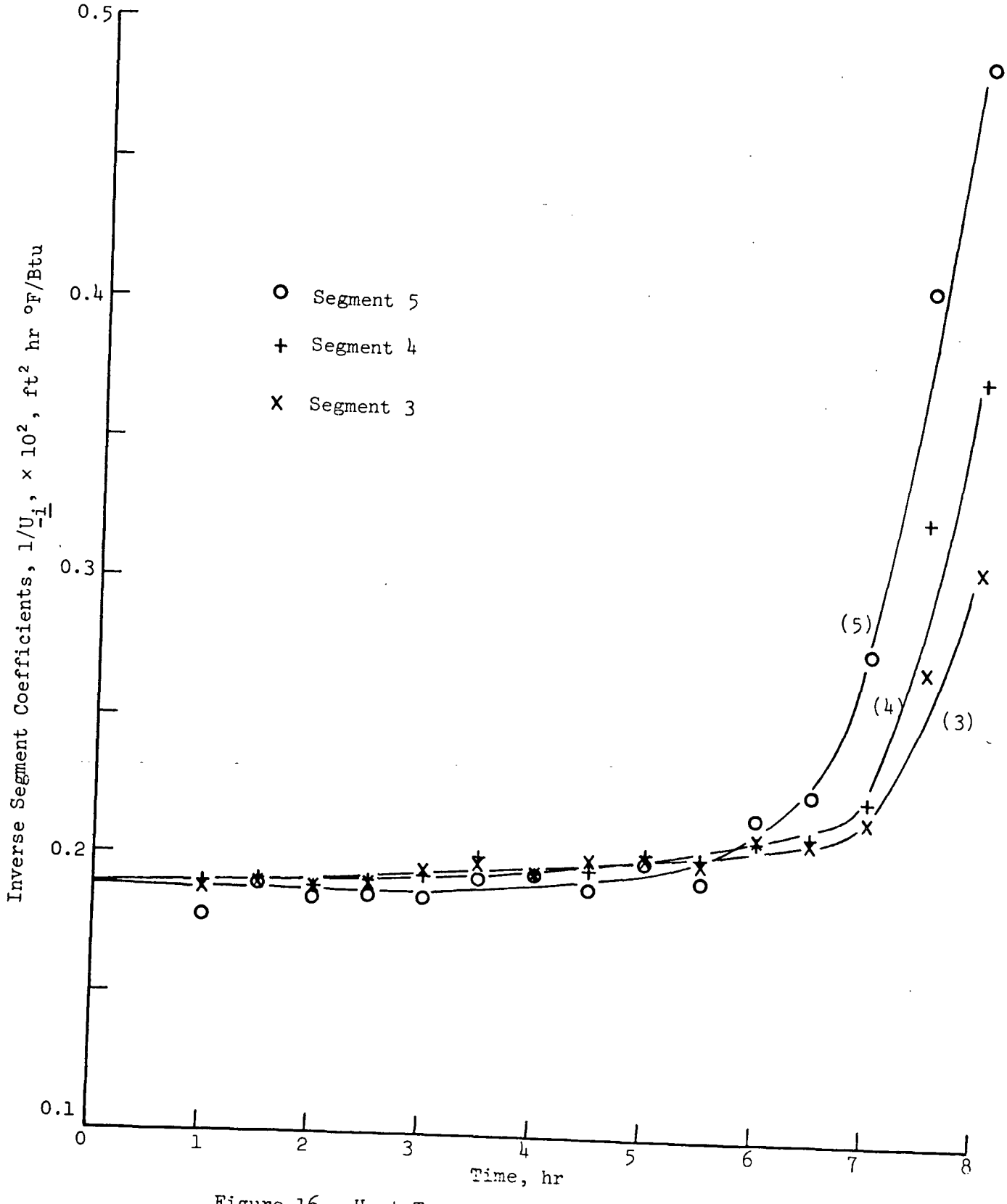

Figure 16. Heat Transfer Resistances in Experiment 6

scaling set in in the previous experiment (Experiment 5). Since the only difference between the two liquors is the fiber added in Experiment 5, it is clear that the same solubility limit is involved.

Summary

The results of this experiment were comparable to those found in previous runs. Scaling set in rather sharply when a critical solids content (determined by the solubility of carbonate and sulfate in the liquor) was exceeded and grew rapidly as solids were increased beyond the critical value. This was not changed by increasing the flow rate by a factor of three and eliminating the subcooled zone. Scaling still set in at essentially the same liquor solids content. It appears unlikely that soluble scale growth can be prevented by any combination of operating variables if the saturation solids content of the liquor is exceeded by more than one or two percent.

SUMMARY OF EXPERIMENTAL RESULTS

The formation of soluble sulfate-carbonate scales is controlled by bulk solubility considerations. Scaling sets in at a rather sharply defined "critical" solids content of the liquor, and rapid growth occurs when this "critical" solids content is exceeded by as little as a percent or so. The "critical" solids content for the onset of carbonate-sulfate scale formation is directly related to the solubility limits of Na_2CO_3 and Na_2SO_4 in the liquor. The solubility curves for Na_2CO_3 and Na_2SO_4 in black liquor presented in Fig. 1 and 2 of this report provide a reliable estimate of the solids content at which scaling can be expected. Scaling is governed by bulk liquor conditions rather than by local conditions at the hot surface.

The concept of potential scale is useful in estimating the severity of a given operating condition. Potential scale is the difference between the amount of scale-forming substances entering the evaporator and that which could leave as a saturated solution at the discharge conditions. Negative values indicate that the discharge concentration is below saturation and so scale formation would not be expected. Positive values of potential scale indicate the likelihood of scale formation. The rate of scale deposition would be expected to increase as the potential scale increased. The results of these experiments indicate that from 5 to 20% of the potential scale is deposited on the tube walls. The fraction of the potential scale which actually forms appears to be related to the residence time in the tube and hence on local longitudinal velocities.

There was no indication in any of the experiments that it was possible to operate in a supersaturated mode without scaling. The small differences between the saturation solids content of the liquor found from solubility considerations and the solids content at which scaling began is less than the uncertainty in the solubility limits and in the local solids contents. If it is possible to operate in a supersaturated mode at all, without scaling, it is only for relatively low degrees of supersaturation which would exceed the saturation solids content by no more than a percent or so.

The effect of evaporator operating variables on scale formation can be explained by their effect on the local solids contents within the evaporator. There was no indication that carbonate-sulfate scales could be controlled by any combination of operating variables alone if the solids content of the liquor was beyond the saturation value. At best, it appears that scaling rates might be reduced somewhat by minimizing residence times in the evaporator once the

critical solids content is exceeded. Since scaling is governed by bulk conditions rather than local conditions, wall temperatures have little effect. It is important to recall that carbonate-sulfate precipitation is a concentration dependent rather than a temperature dependent phenomenon.

Fiber in the liquor did not appear to have a major effect on carbonate-sulfate scaling. The fibers do get preferentially incorporated into the deposit and do affect the morphology. The scale is much rougher when fiber is present. It would also be expected to have more bulk. However, the growth of scales is still essentially governed by bulk solubility considerations. The presence of fiber in the liquor does not lead to scale growth at solids contents below the saturation value for the liquor. It is likely that scales grow more rapidly once the critical solids content is exceeded, but this does not seem to be that important. Even without fiber, scales can grow very rapidly if the liquor is concentrated more than a percent or so beyond the critical value. It is possible that fiber has a much greater influence in a commercial evaporator in which there are many tubes in parallel than it did in this program with a single-tube evaporator. This point is discussed more thoroughly later in this report.

All of these experiments were carried out with new 304 SS tubes. In all cases in which the critical solids of the liquor was exceeded, scales formed. There did not appear to be any problem of scales adhering to the tube surface. There was no evidence for an induction period to permit slow growth of a surface layer before rapid growth could occur. Since scales form readily under the conditions used in these experiments, it is unlikely that the presence of a layer of an insoluble deposit would have a major influence on soluble scale.

The overall heat transfer rate in these types of evaporators (LTV's) is strongly dependent on the fraction of the tube surface needed to supply the sensible heat load (the subcooled length). Heat transfer rates are much lower in the subcooled zone than in the net boiling zone. In almost every experiment carried out, initial heat transfer rates in the subcooled zone were relatively high and then proceeded to drop off with time. This decay in heat transfer in the subcooled zone was not due to scaling in the usual sense since negligible amounts of scale were found in that area. The initial high values of the subcooled heat transfer are believed to be due to subcooled boiling. This is nucleate boiling at the hot surface where the boiling point of the liquor is exceeded followed by rapid collapse of the vapor bubbles as they move into the cooler bulk liquor. The decay in the heat transfer rate is apparently due to the gradual suppression of subcooled boiling and a greater reliance on convection. The reasons for this are not clear at this point. Whatever the reason, this decline in heat transfer rate in the subcooled zone affects the overall heat transfer coefficient just as if the evaporator is scaling, even if it has little or nothing to do with deposits forming.

APPLICABILITY TO COMMERCIAL EVAPORATORS

The main difference between the experimental system used in this study and commercial LTV evaporators is that this system used a single tube while commercial evaporators have many tubes in parallel. This is not a negligible difference. The flow within the tubes is governed by different conditions in the two cases.

The single-tube evaporator is essentially a constant flow system. Liquor is pumped into the evaporator tube at a constant, predetermined rate which is essentially independent of the processes occurring within the evaporator. A single tube in a commercial LTV evaporator, on the other hand, sees

a constant pressure drop environment. The flow through that tube is dependent on the flow resistance of that tube and the boiling processes within it. It is entirely possible that stationary flow patterns are not realized and that the flow through the tube is oscillatory.

In view of these differences between the experimental evaporators and commercial systems, care must be taken in applying the results of this study. The basic findings summarized in the preceding section are not in doubt. Scale formation is governed by bulk solubility considerations and sets in when the bulk liquor solids content exceeds the critical solids content of that particular liquor. The effect of operating variables can be interpreted in terms of their effect on the bulk solids content. However, these results cannot be applied too literally. In the commercial evaporator, operating variables could affect the flow through a given tube. The instantaneous flow rate has a strong effect on the solids content as shown by the heat balance below.

$$W_f \left\{ C_p (T_{Lo} - T_{Lin}) + \lambda \frac{(S_o - S_{in})}{S_o} \right\} = Q \qquad (7)$$

where

W_f = liquor feed rate

C_p = heat capacity

T_{Lo} = temperature of liquor out

T_{Lin} = temperature of liquor in

λ = heat of vaporization

S_o = solids content of liquor out

S_{in} = solids content of liquor in

Q = heat transfer rate

Thus, the consideration of the effect of operating variables on scaling in commercial evaporators must be based on their effect on flow rates and flow stability.

It is likely that the effect of fiber in the liquor is much greater in commercial evaporators than in the single-tube system. Fiber in the liquor will affect the rheological properties of the liquor. In addition, the rougher scale would increase the flow resistance. Thus, if a fiber-bearing scale forms in an evaporator tube, the greater flow resistance will lead to less flow in that tube and thus generally higher solids levels. This increases the likelihood of added scale growth. This process could feed on itself with the ultimate result being a plugged tube.

PREVENTION OF CARBONATE-SULFATE SCALE

The experimental study of soluble scale formation just discussed identified the factors which control the scale-forming process. These results provide a rationale for controlling these types of deposits in the field. The task remaining is to use this information to develop measures that will control or prevent the formation of carbonate-sulfate scales. This subject is discussed in this section.

CHANGES IN LIQUOR COMPOSITION

Since the scaling process is controlled by bulk solubility considerations, it is appropriate to examine the factors which control carbonate-sulfate solubility and see what changes could be made in liquor composition which would increase the solids content at which saturation is reached. The general solubility behavior of Na_2CO_3 and Na_2SO_4 is summarized in Fig. 1 and 2 presented earlier in this report. To a first approximation sulfate and carbonate can be considered together. The main liquor composition parameters which affect solubility limits are the sum of Na_2CO_3 and Na_2SO_4, and the effective sodium content of the liquor. The latter is all of the sodium other than that accounted for by the Na_2CO_3 and Na_2SO_4 and is calculated as the difference between the total sodium content and the sodium present as Na_2CO_3 and Na_2SO_4. Increased Na_2CO_3 + Na_2SO_4 values decrease the saturation solids content of the liquor because the saturation Na_2CO_3 + Na_2SO_4 to water ratio is reached at lower solids contents. Increased values of effective sodium decrease the critical solids content because of a common-ion effect. There is an additional dependence of the solubility limit on the carbonate/sulfate ratio. The solubility limit tends to decrease as the proportion of sulfate increases. This effect is relatively small.

The most direct method of increasing the critical solids content of the liquor is to reduce the amount of Na_2CO_3 and Na_2SO_4. The effect of such a reduction can be determined from the solubility curves. In the region around 50% solids, a reduction in the Na_2CO_3 + Na_2SO_4 content of 1% (e.g., from 20% on the solids to 19%) will increase the saturation solids content by about 0.9% (e.g., 48 to 48.9%). Depending on the particular situation this may be very beneficial. A reduction in sulfate and carbonate load could increase the saturation solids content enough to eliminate the problem. According to the survey, most mills have a saturation solids content over 50% solids. The average value was 52.9%. Those few mills which have Na_2CO_3 + Na_2SO_4 values above 15% on the solids would certainly seem to have the capability of making a significant reduction in carbonate and sulfate content. This would raise the critical solids content by a comparable amount.

The main origin of sulfate in black liquor is incomplete reduction in the recovery furnace. Thus, the sulfate content of the black liquor can be lowered by increasing the reduction efficiency of the furnace. For example, an increase from 85 to 90% in reduction efficiency would cut the sulfate load in the black liquor to 2/3 of its original value. In addition, sulfate should not be added to weak liquor. This would include spent ClO_2 generator acid, brines from SO_2 scrubbers or other wet scrubbers, and other miscellaneous sources of sulfate. Neutral sulfite semichemical liquor or other sulfur based semichemical liquors can be a significant source of sulfate if they are blended with the kraft weak liquors and evaporated jointly.

Carbonate in black liquor stems mainly from the carbonate in the white liquor and that produced by chemical reactions during the cook. The former can be lowered by increasing the conversion efficiency in the causticizing operation.

In addition, miscellaneous sources of Na_2CO_3 should be kept out of weak liquor if at all possible.

Reducing the amount of carbonate and sulfate in the black liquor can be an effective means for controlling soluble scale. However, it must be remembered that reducing the carbonate-sulfate load does not eliminate the possibility of precipitation. It only increases the solids level at which precipitation will occur. If the solids level in the evaporator exceeds the saturation solids content, scaling is still likely. If the solids content leaving the evaporator is below the saturation solids content of the liquor and soluble scale is still being formed, it indicates internal flow stability problems, and a reduction in the carbonate-sulfate content of the liquor may not alleviate the scaling problem.

The solubility curves in Fig. 1 and 2 should be used as guidelines only and not be interpreted as absolute solubility curves valid for all liquors. They are an average of the solubility behavior of a number of black liquors. Individual liquors can deviate from these curves. Direct measurement of saturation levels in any particular liquor would be more reliable than the general curves. Unfortunately, solubility measurements in high solids liquors are quite difficult to make. Thus, in many cases, Fig. 1 and 2 would be the only information available.

Addition of caustic to black liquor increases the effective sodium content of the liquor and decreases the saturation solids content. It lowers the solubility of Na_2CO_3 and Na_2SO_4 by increasing the concentration of the sodium common-ion. This effect of caustic addition has been verified in solubility tests as well as in the single-tube evaporator studies. Caustic addition, or high residual active alkali, will not prevent carbonate-sulfate scaling. A minimum

amount of active alkali is needed to prevent lignin precipitation. Apparently, the liquors used in this study exceeded this minimum, as there was no evidence of lignin precipitation in any of the runs. Hence, about 5% RAA on the solids (as Na_2O) or about 8 gpl in weak liquor seems to be adequate. It remains to be established if high RAA values above this amount are effective in preventing other types of scales.

Fiber should be kept out of the liquor to the maximum extent possible. Fiber does not affect the solubility behavior in the system, and hence, the solids content at which scaling would be likely to begin. However, fiber does get incorporated into the scale, increasing its bulk and creating a rougher surface. This is likely to affect flow distribution in the evaporator and could enhance tube plugging problems. Fiber filters can be used to prevent fibers from getting into the evaporators. Problems caused by fibers can be almost totally eliminated by installing a filter in the weak liquor system upstream of the evaporators, and their use is strongly recommended. The type of experiments carried out on this program could not possibly provide guidelines for the safe level of fiber in black liquor, or the fiber concentration at which trouble should be expected. These would have to be based on mill experience.

Polymeric additives would not be expected to have much effect on carbonate-sulfate scaling. Sodium carbonate and sulfate constitute from 10 to 20% of the total liquor solids. The amount of material which could form scale is so great that complexing agents or protective colloids would not be expected to be effective unless massive dosages were used. Organic agents which would absorb on the wall and serve to block attachment of the scale might work; however we are not aware of any such use for carbonate-sulfate scale prevention.

EVAPORATOR OPERATION

The simplest way to prevent soluble scale is to operate the evaporator so that the discharge solids is below the saturation concentration. This is, in fact, done and is the main reason why the soluble scale problem is not more serious than it presently is. The usual goal in the multiple-effect evaporators is to concentrate the liquor to about 50% solids. Most black liquors become saturated in sulfate-carbonate at about this same solids level. If the saturation solids content of a given liquor is lower than normal, the solids content reached in the evaporator can be reduced by a corresponding amount so as to prevent soluble scale from forming.

Prevention of soluble scale by limiting the extent of concentration in the evaporator is a feasible approach as long as there is sufficient capacity in the direct contact evaporator or concentrator system to complete the evaporation. There will be a slight energy penalty because the efficiency of energy use (steam economy) is normally greater in the multiple-effect evaporators than in the other systems.

The results of the experiments with the single-tube evaporator indicated that evaporator operating variables had little effect on carbonate-sulfate scaling other than through their effect on liquor solids content. Those conditions that produced solids contents greater than the saturation value were prone to scale. Those conditions which did not increase the solids content beyond the saturation level did not scale. There was no indication that any combination of operating variables would permit stable operation in the supersaturated regime, without scaling. It did appear that high throughput velocities which reduce the residence time of liquor in the tubes led to scaling rates which were a smaller fraction

boiling occurring at the hot surface and being gradually suppressed. The reason for suppression is not known. It is apparently not linked to carbonate-sulfate scale formation, since little or no scale was found in this region. However, this behavior would affect the overall heat transfer coefficient in a way which would mimic scaling. If this behavior is generally characteristic of black liquor LTV evaporators, then substantial improvement in heat transfer coefficients and less degradation in performance could be expected if sensible heat requirements were met before the liquor was introduced into the LTV evaporator.

Flow stability is an important consideration. This includes stability of the overall flow into the evaporator and flow stability within the individual tubes. The solids content reached in an evaporator is an inverse function of the flow into it.

$$S_o = \frac{S_{in}}{1 + \frac{C_p (T_{Lo} - T_{Lin})}{\lambda} - \frac{Q}{W_f \lambda}} \qquad (9)$$

Thus, if the liquor flow rate is variable, conditions may exceed the saturation level part of the time. Or, if the total feed is not uniformly distributed over all of the tubes, the solids content would tend to be higher in some tubes than in others. This tendency toward inequitable flow distribution could be self-propagating. As scale begins to form in a tube its flow resistance would tend to increase, and this could accentuate the maldistribution of the flow. The experimental data obtained in this study does not provide answers to questions of flow stability. This is a complex question of two-phase flow stability, and the effect of macroscopic operating variables on stability is unknown at the present time.

In an actual multiple-effect evaporator system, freedom to choose operating variables is rather limited because of the interlinking of the effects. Thermal driving forces are basically set by the choice of the number of effects, steam temperature and condenser temperature. Of these, only the steam temperature is an effective operational variable. The sensible heat load depends on the weak liquor temperature, number of effects, liquor flow sequence, and the use of auxiliary heaters, internal preheaters and afterheaters. The amount of subcooling of the liquor entering any given effect is a manipulatable variable. The weak liquor feed rate to the evaporator is governed by factors external to the evaporators and is not manipulatable over the long run. The flow of liquor to any particular effect (or the liquor velocity) can be varied by using multiple-pass arrangements or by recirculating some of the concentrated liquor. The pressure in the vapor heads is directly coupled with the thermal driving forces and is not directly controllable. It is possible to select the pressure and temperature level for the high solids effect by appropriate choice of the feed sequence.

Overall operational stability of the entire multiple effect system would be expected to have an effect on carbonate-sulfate scaling, since it could lead to periods of high solids content which could cause scales to form. Thus, the evaporator control system is important. In the experiments carried out in this study, scaling took place most rapidly when the system was forced to maintain a discharge solids content above the critical value. Scaling was more gradual and tended to be self-limiting when the steam temperature was held constant and the heat transfer rate allowed to fall off as scaling proceeded. Another aspect of evaporator control systems which would have a bearing on scale formation is whether steady operation can be maintained. Upsets could lead to locally high solids values and scale formation.

BULK CRYSTALLIZATION

Since precipitation of carbonate and sulfate from black liquor occurs because the liquor is concentrated beyond the saturation limit rather than by temperature effects, there is no inherent reason for scales to grow on the wall. The precipitation process can be considered to consist of two steps, formation of a supersaturated solution by concentration of the liquor, and precipitation of solids with the degree of supersaturation as a driving force. The system will tend to relieve itself of the supersaturation by the carbonate and sulfate coming out at interfaces between solid phase and the solution. These interfaces may be at the tube surface. They could also be carbonate-sulfate crystals entrained in the liquor. If the growth on entrained crystals is rapid enough, the degree of supersaturation can be kept low enough to minimize or eliminate precipitation (scale formation) on the tube surface. Since the rate of solid precipitation would be proportional to the exposed surface area (for a given driving force), the main criterion for favoring bulk crystallization over scale growth on the wall would be the relative amount of exposed area.

Entrained carbonate-sulfate precipitate would not be expected to cause problems during evaporation so long as it does not settle out of the liquor. The high liquor solids contents needed to reach saturation and the tendency for liquor viscosity to increase strongly with increasing solids content will help to keep the entrained solids in suspension. Stagnant liquor zones would have to be avoided so that the entrained solids would not settle out. These could occur in the subcooled part of the evaporator or in liquor transfer piping. It could particularly be a problem in heavy liquor storage tanks.

Provision for bulk crystallization could be made either by adding solid Na_2CO_3 and Na_2SO_4 to act as seed crystals or by recirculating heavy black liquor

containing bulk carbonate-sulfate crystals. The point of addition could be critical. The degree of saturation changes rapidly with solids content in the region of the saturation solids content. If the solids content is too low, the bulk crystals will tend to dissolve. On the other hand, if the liquor is concentrated beyond the saturation solids content before the solid phase is added, scaling could take place in the preceding concentration step. The ideal situation would be to take a liquor which was unsaturated and add enough solid or recirculated liquor to take it above the saturation solids content. The solubility curves could be very useful in selecting conditions which will give this.

Since the basic cause of carbonate-sulfate scaling is concentrating the liquor beyond the critical solids point in the presence of the heat transfer surface, it should be possible to prevent this type of scale by separating the concentration step from the heat transfer step. This could be done by operating the evaporator in a flashing mode. Heat transfer could be entirely into liquid phase to raise the sensible heat content followed by a reduction in pressure and flashing. Precipitation of solids would then take place in the flash chamber, presumably in bulk, and not on the heat transfer surface. A similar effect can be achieved by using high liquor recirculation rates. The concentration of the feed liquor to the evaporator is effectively raised when it is mixed with the higher concentration recirculating liquor. The concentration increase, for the same total heat transfer rate, along the tube becomes progressively less as the fraction recirculated increases. Thus, high recirculation would be expected to greatly reduce the tendency to form soluble scales, both by providing carbonate-sulfate crystals to serve as growth sites and by minimizing the concentration increase along the tube.

SURFACE CONDITIONS

It appears unlikely that soluble carbonate-sulfate scales can be controlled through adjustments of tube surface conditions. In this work scales were easily grown on new, clean evaporator tubes. There was no indication of an induction period or a need to first form a layer of scale by a slow, nucleation controlled process before rapid scale growth would occur. This suggests that surface conditions are not that important a variable. This implies that the growth of carbonate-sulfate scales will not be influenced significantly by whether or not the tube surface is clean; the magnitude of heat transfer coefficient will be affected, but not the scaling rate (for a given degree of supersaturation). A previous deposit could have an influence through the change in heat transfer distribution. If a nonuniform deposit is present, and the overall ΔT increased to reach a desired heat transfer rate, the distribution of heat flux along the tube could be different and this could influence the behavior.

Organic additives might have some beneficial effect if they could be absorbed on the tube surface and then prevent the deposit from adhering to the wall. They would have to be able to do this in a fairly strongly alkaline environment. Low energy surfaces might also be effective, but it would have to be possible to maintain the low energy surface intact for long durations for this approach to be effective. In general, control of surface conditions does not appear to be an effective approach to control of soluble carbonate-sulfate scales.

DETECTION AND IMPACT

In an operating evaporator, scale would have to be detected by the effect of scale in the heat transfer resistance. This can be done by following

the heat transfer coefficient as a function of time. The heat transfer coefficient in any given effect is given by,

$$U_i = Q_i / A_i \Delta T_i \qquad (10)$$

where

U_i = heat transfer coefficient for ith effect, Btu/hr ft^2 °F

Q_i = heat transfer rate in ith effect, Btu/hr

A_i = heat transfer area in ith effect, ft^2

ΔT_i = thermal driving force in ith effect, °F

The thermal driving force, ΔT_i, is by convention taken to be the difference between the saturation temperature of the heating steam in the ith effect and the boiling temperature of the liquor in that effect. Its value can be found by direct measurement of these quantities. The heat transfer area is fixed by the evaporator geometry. The heat transfer rate can be found from a heat balance on the ith effect,

$$Q_i = W_{Li} \left\{ C_p \left(T_{Lo} - T_{Lin}\right) + \lambda \frac{\left(S_o - S_{in}\right)}{S_o} \right\}_i \qquad (11)$$

where W_{Li} in the liquor flow rate into the ith effect and temperatures and solids in and out are for the ith effect. Alternatively, the heat transfer rate could be found by measuring the steam (vapor) flow to the ith effect.

$$Q_i = W_{si} \lambda_{si} \qquad (12)$$

where W_{si} is the flow of heating steam to the ith effect and λ_{si} is the heat of vaporization of water at the conditions existing in the steam side of the ith effect.

If neither the liquor flow rate or steam flow rate to the ith effect is measured, it is necessary to estimate the heat transfer rate. This can be

done by making use of the approximation that the heat transfer rate in a multiple-effect evaporator is the same in each effect. This assumption and an overall heat balance can be used to give

$$Q_i = \frac{W_{WL}\, C_{pWL}\, (T_{SL} - T_{WL}) + W_e \lambda}{N} \qquad (13)$$

where

W_{WL} = weak liquor feed to evaporator system

C_{pWL} = specific heat of weak liquor

T_{SL} = temperature of strong liquor out

T_{WL} = temperature of weak liquor

W_e = amount of water evaporated

N = number of effects

The heat of vaporization, λ, is evaluated at the pressure of the strong liquor being discharged.

Heat transfer rates are highly coupled in a multiple-effect evaporator. As heat transfer coefficients change, thermal driving forces adjust themselves over the various effects in accordance with heat balance restrictions. This can be treated quantitatively, in a simplified manner, by assuming equal heat transfer rates in each effect; i.e., $Q_k = Q_j$. With this assumption,

$$U_k A_k \Delta T_k = U_j A_j \Delta T_j \qquad (14)$$

Thus, the relation between the temperature driving forces is

$$\Delta T_j = \frac{U_j A_j}{U_k A_k} \Delta T_j \qquad (15)$$

It is possible to define an overall driving force, ΔT_o, by

$$\Delta T_o = T_s - T_c - \Sigma \text{ b.p. rise} \qquad (16)$$

where

ΔT_o = overall thermal driving force for multiple-effect system

T_s = saturation temperature of steam supply

T_c = condensing temperature of vapor leaving final effect

Σ b.p. rise = sum of boiling point rise in each effect

The overall driving force is related to the individual driving forces by

$$\Delta T_o = \sum_{k=1}^{N} \Delta T_k \qquad (17)$$

Under these conditions, the total heat transfer rate is related to the overall thermal driving force by

$$Q_T = \frac{N\ \Delta T_o}{\left\{\frac{1}{U_1A_1} + \frac{1}{U_2A_2} + \ldots + \frac{1}{U_NA_N}\right\}} \qquad (18)$$

This equation can be used to estimate the effects of changing coefficients (due to scaling) on the total heat transfer rate (proportional to evaporator capacity). It should be noted that the denominator consists of inverses of coefficient-area products. Thus, the effects having lowest values of U_kA_k tend to control the total heat transfer rate. The total heat transfer rate is determined by the sum of the effective resistances of each effect ($1/U_kA_k$), and this helps to prevent extremely rapid drops in the total heat transfer rate as a given effect scales. The thermal driving force spontaneously increases over the scaling effect and decreases over the others. For example, if we have a 6-effect evaporator and the initial values of U_kA_k are the same for each effect, and the coefficient in the first effect is then cut in half, the total heat transfer rate would be 6/7 of the initial value. If scaling is confined to a single-effect (as it would be expected to do for carbonate-sulfate scaling) rather large drops in the coefficient for that effect

could be tolerated before it is impossible to maintain the desired heat transfer rate by increasing ΔT_o.

CONCENTRATOR OPERATION

One final matter must be addressed in considering how the results of this study apply to evaporation in mill situations. This has to do with concentrators, the steam heated evaporators which are used to concentrate liquors from the 50% or so solids contents leaving the multiple-effect evaporators to firing concentration (about 65% solids). The relationship between carbonate and sulfate content of liquor and critical solids content is such that essentially all concentrators exceeding 60% solids operate beyond the saturation limit. Hence, all concentrators operate in a region of positive potential scale. How are they able to operate?

Several different techniques can be used to concentrate liquors well beyond the saturation point without encountering serious scaling problems. These include:

1. Recirculating concentrated liquor to provide carbonate-sulfate crystals in the bulk liquor as preferred sites for precipitation.
2. Minimizing the degree of concentration of liquor along the tube.
3. Eliminating stagnant liquor areas.
4. Providing positive flow within individual tubes.
5. Providing for easy removal of scale by water or weak liquor washing.

6. Providing a relatively large amount of heat transfer surface for the required heat duty, so that operation can be continued with significant amounts of scale.

Commercial concentrator designs involve one or more of these steps. Concentrators are an example of how scales caused by precipitation of a major liquor component at high solids content can be prevented or lived with.

CONCLUSIONS

Water soluble, sulfate-carbonate scales can form during evaporation of kraft black liquor. The deposits form by precipitation of Na_2CO_3 and Na_2SO_4 from a supersaturated solution which forms as the liquor is concentrated beyond the saturation level. Scale growth is governed by solubility conditions in the bulk liquor rather than by local conditions at the hot surface. Scaling sets in at a critical solids content, dependent on liquor composition, and can become quite rapid as the critical solids content is exceeded.

Solubility curves for Na_2CO_3-Na_2SO_4 in black liquor, developed in a preceding study and presented in Fig. 1 and 2, have proven useful in estimating the critical solids content of the liquor. The concept of potential scale can be used to evaluate the severity of scaling which might be encountered. Potential scale is the difference between the rate at which scaleable substances are entering the evaporator and the rate at which they could leave as a saturated solution at the discharge solids content. Potential scale increases very rapidly once the saturation solids content is exceeded.

The effect of liquor composition on scaling was in accordance with the effect of liquor composition on solubility limits. The saturation solids content is lowered by increasing amounts of carbonate and sulfate in the liquor, increased levels of sodium common-ion, and increased proportion of sulfate. The addition of NaOH to the liquor to maintain a high residual active alkali in the liquor did <u>not</u> prevent scale formation. No benefits of high residual alkali on carbonate-sulfate scaling were evident.

The effect of evaporator operating variables on carbonate-sulfate scaling is directly related to the effect of these operating variables on local

solids content. There was no indication that stable supersaturation could be maintained without scaling through proper choice of operating variables. In an LTV evaporator, it does not appear that carbonate-sulfate scaling can be controlled by operating variables alone, if the system is operated beyond the saturation level.

The results of these experiments were obtained with a single-tube evaporator with positive liquor feed to the tube at all times. Commercial LTV evaporators, with many tubes in parallel, are much more sensitive to flow variations within the tube. These variations can give rise to intermittent solids levels above the saturation level, and hence scale formation. Thus, commercial LTV evaporators may be sensitive to operating or composition variables (which would affect flow stability) that were not found to be critical in the present program. Fiber in liquor appears to be a variable of this type.

The overall heat transfer coefficient was found to be strongly dependent on the fraction of the tube surface needed to supply the sensible heat requirement. Local coefficients are much lower in the subcooled zone than they are in the net boiling zone. A substantial improvement in overall heat transfer coefficient could be obtained by shortening or eliminating the subcooled zone (provided that this does not adversly affect flow stability). In practically all of the runs, the heat transfer coefficients in the subcooled zone were relatively high initially and then dropped off with time. This decay in heat transfer coefficient is apparently due to a gradual suppression of subcooled boiling. It does not appear to be due to formation of macroscopic amounts of deposits, although it will masquerade as scaling in that it will cause the overall heat transfer coefficient to decrease with time.

Carbonate/sulfate scaling in black liquor evaporators can be readily prevented or minimized. The following steps can be used to achieve these goals.

1. Reduce the discharge solids content from the evaporator to a level below the saturation solids content of the liquor.
2. Reduce the amount of sulfate and carbonate in the liquor so that the saturation solids content is raised to a level greater than the discharge solids content. Reduction in sulfate levels is somewhat more beneficial than reduction of carbonate.
3. Install a fiber filter in the weak liquor line to keep fibers out of the black liquor.
4. Maintain operation as stable as possible. Avoid cycling of flow rates, etc.
5. Provide seed crystals to encourage precipitation in the bulk liquor rather than on the heat transfer surface. This can be done by recirculating heavy liquor containing precipitated carbonate and sulfate.

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NOMENCLATURE

A = heat transfer area, ft^2

A_s = heat transfer area of one segment, ft^2

C = concentration of a scaleable substance, lb/lb solids

C^* = saturation concentration of scaleable substance, lb/lb solids

C^{**} = saturation concentration expressed as lb/lb H_2O

C_p = specific heat, Btu/lb °F

D = tube diameter, ft

K = proportionality constant in Equation (1), lb Btu/hr ft^2 °F

K = proportionality constant in Equation (33), °F or °C

L = tube length, ft

L_s = length of a single segment, ft

$\dot{M}$ = rate of scale formation, lb/hr

N = number of evaporator effects

P = pressure, psi

PS = potential scale, lb/hr

Q = heat transfer rate, Btu/hr

R = scaling rate as determined from heat transfer data, ft^2 °F/Btu

S = liquor solids content

T = temperature, °F or °C

T_c = condensing temperature of liquor leaving last effect, °F

T_s = steam temperature, °F

T_{sw} = saturation temperature of water at local pressure, °F or °C

ΔT_o = overall thermal driving force = $T_s - T_{L5}$, °F

ΔT_i = thermal driving force in ith effect, °F

ΔT_{sc} = extent of subcooling, = $T_{L5} - T_{Lin}$, °F

$\underline{U}$ = heat transfer coefficient, Btu/hr ft^2 °F

$\underline{U_B}$ = heat transfer coefficient based on average boiling temperature, Btu/hr ft^2 °F

$\underline{V}$ = vapor velocity, ft/hr

$\underline{W}$ = flow rate, lb/hr

$\underline{W_e}$ = evaporation rate, lb/hr

$\underline{W_f}$ = feed rate, lb/hr

$\underline{W_s}$ = steam flow rate, lb/hr

$\underline{W_v}$ = vapor flow rate, lb/hr

$\underline{W_v}$ = rate of condensed vapor out of evaporator, lb/hr

$\underline{W_{vent}}$ = loss of water vapor out vent, lb/hr

$\underline{W_{WL}}$ = weak liquor flow rate, lb/hr

$\underline{Z}$ = position coordinate, positive in upward direction with origin at the tube bottom, ft

$\underline{g}$ = gravitational acceleration, ft/sec^2

$\underline{h_c}$ = condensing side film coefficient, Btu/hr ft^2 °F

$\underline{h_L}$ = liquor side film coefficient, Btu/hr ft^2 °F

$\underline{k_s}$ = thermal conductivity of scale, Btu/hr ft °F

$\underline{k_w}$ = thermal conductivity of tube wall, Btu/hr ft °F

$\underline{t}$ = time, hr

δ_s = scale thickness, ft

δ_w = tube wall thickness, ft

λ = heat of vaporization, Btu/lb

ρ = density, lb/ft^3

θ = boiling point rise, °F or °C

Subscripts

CL = concentrated liquor leaving evaporator

in = inlet condition

i = designates ith segment. For point variables it denotes conditions at end of segment

j,k = designate jth and kth effects

L = liquor or liquid phase

o = outlet condition

SL = strong liquor

T = total, value for the whole evaporator

V = vapor

WL = weak liquor

* = end of subcooled zone

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APPENDIX I

DESCRIPTION OF EXPERIMENTAL EVAPORATOR SYSTEM

Experimental measurements of scaling behavior were made on a single-tube evaporator system designed to permit control of operating variables over a wide range, accurate measurement of the heat transfer behavior, and access to the scale formed.

SINGLE-TUBE EVAPORATOR

The evaporator itself is a vertical shell and tube heat exchanger with a single 304 SS tube, 2 inches in diameter and 19 feet plus in length. The shell is divided into five segments, each 3.8 feet long, to permit measurement of the heat transfer distribution along the tube. A schematic diagram of the single-tube evaporator is shown in Fig. 17.

A detailed diagram of a single segment is shown in Fig. 18. The shell itself consists of a 6-inch diameter stainless steel tube welded to two flanges. The top flange has a full 6-inch diameter opening, while the bottom flange contains a hole slightly greater than 2-inch diameter to permit the evaporator tube to pass through. The distance from the top of the top flange to the bottom of the bottom flange is 46 inches.

A guard ring, made from a 4-inch diameter stainless steel tube 18 inches long, is welded to the bottom flange. This separates condensate which forms on the outside of the evaporator tube (which is directly related to the heat transfer rate) from that which forms on the shell (heat loss to the surroundings). A hole is drilled radially inward through the bottom flange to permit drainage of the condensate from inside the guard ring and its subsequent measurement. A top shroud, about 4-3/4 inches in diameter is hung from the packing gland assembly and overlaps

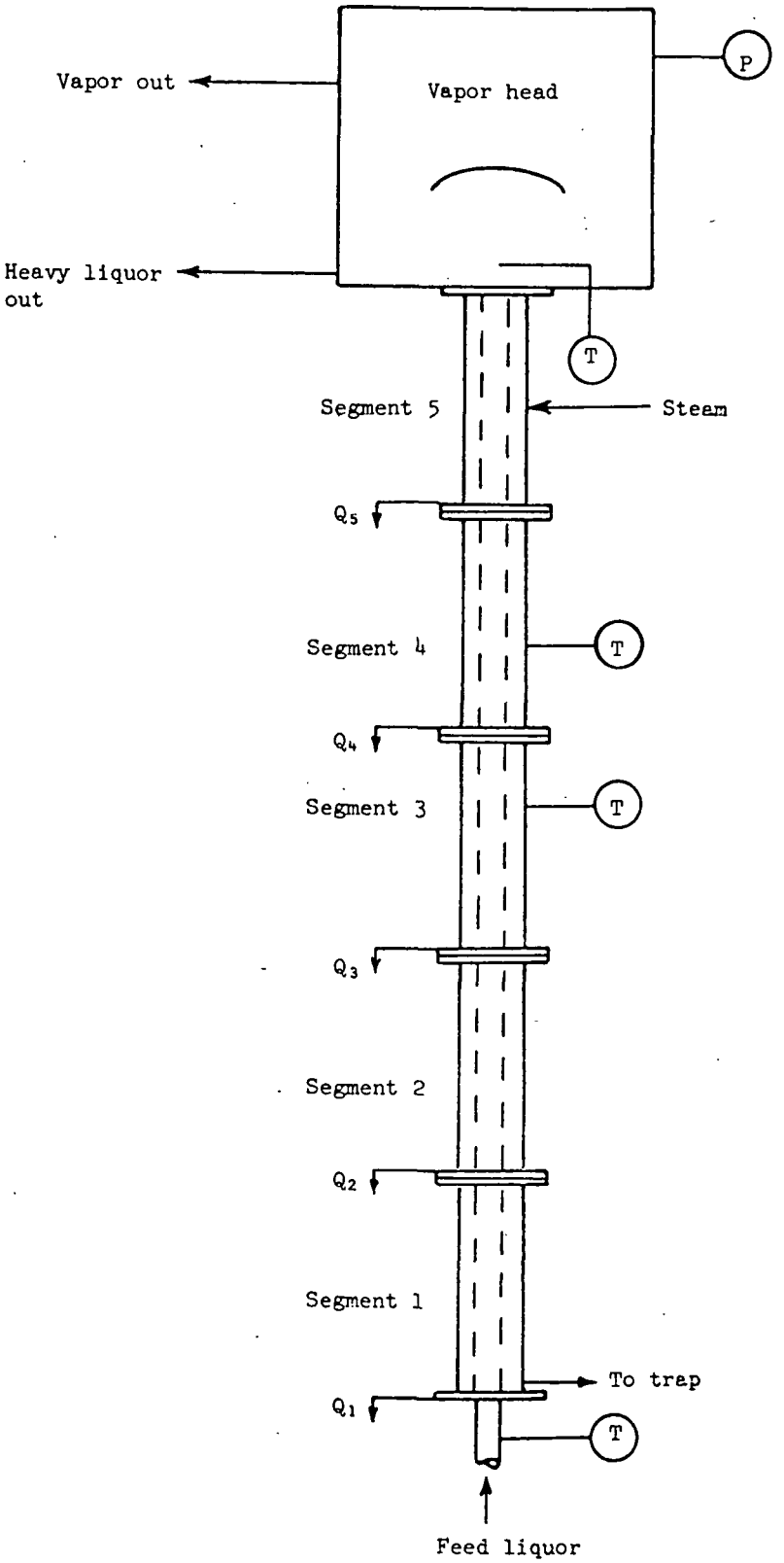

Figure 17. Schematic Diagram of Single-tube Evaporator

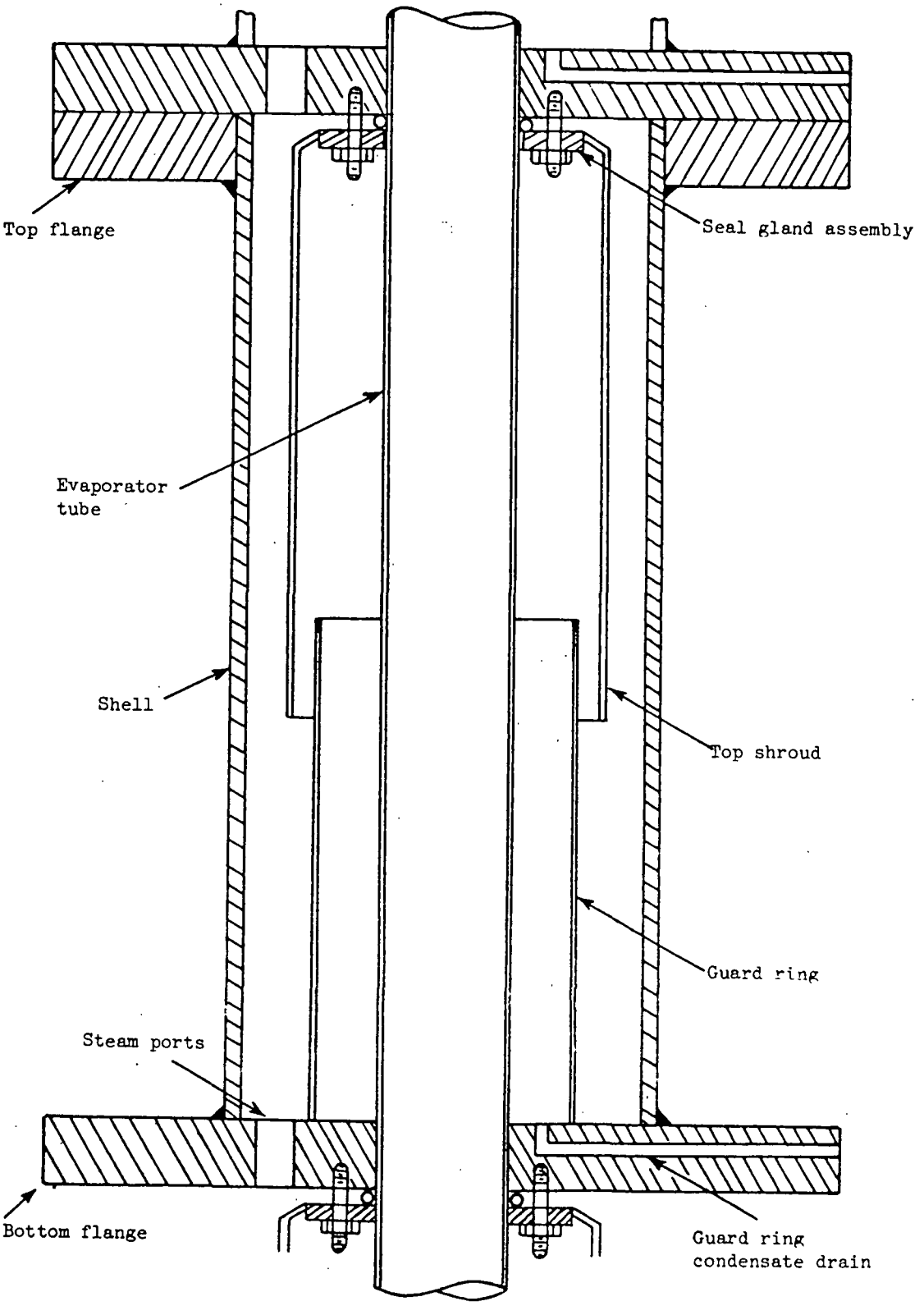

Figure 18. Detailed Diagram of a Single Segment

the guard ring a short distance. This further isolates the evaporator tube from the outside of the shell and prevents entrained condensate from entering the guarded zone. The evaporator tube is in full contact with steam at all times. Cross-sectional areas in the guard zone, between the shroud and the guard ring and between the shell wall and the shroud, are large enough that steam velocities never exceed 10 ft/sec anywhere in the shell space. The whole purpose of these arrangements is to permit an accurate measurement of the rate of heat transfer as a function of position along the evaporator tube.

Steam is supplied to the top segment. The construction of this segment is a little different. No top shroud is used. Instead, the 4-inch diameter guard tube welded to the bottom flange extends up 36 inches (instead of 18). The opening for the steam supply line is located 15 inches down from the top so that the entering steam impinges on the guard tube rather than the evaporator tube. Eight 5/8-inch diameter holes were drilled equally spaced on a 4 7/8-inch diameter bolt circle in all of the bottom flanges except for that in the bottom (1st) segment. These are located in the annular zone between the guard ring and the outside shell. They provide a passage for steam between segments and also allow the condensate that forms on the shell wall to fall to the bottom segment where it is removed through a trap. The open area is sufficient so that steam velocities never exceed 20 ft/sec in passing from segment to segment. The pressure drop from the top segment to the bottom on the shell side is negligible.

The entire evaporator assembly is supported from the vapor head. The tube is rolled into a tube holder, 5 inches in diameter by 5/8 inch thick. This tube holder fits through an opening in the bottom of the vapor head and presses against a stop ring welded to the inside of the vapor head bottom. The necessary pressure is maintained by a dummy flange pressed against the tube holder by the

top flange of the top segment which is bolted to the bottom of the vapor head. Details of this assembly are shown in Fig. 19. The tube and the top segment are mounted first. Then the packing gland at the bottom of this segment is tightened and the top shroud for the next (4th) segment attached. The fourth segment is then brought up from the bottom, bolted to the top segment, its packing gland is then tightened, and the next shroud hung. This procedure is repeated until the entire assembly is together. The packing glands serve as a seal to prevent condensate from one segment from leaking into the one below. The packing gland at the bottom is accessible from the outside and seals against the steam pressure in the evaporator. A flexible tube is used to connect the liquor feed system to the evaporator tube. Hence, the entire assembly is free to expand longitudinally as temperatures are raised.

EVAPORATOR SYSTEM

The complete experimental system includes not only the evaporator itself, but also a liquor feed system, vapor-liquor separator, condenser, discharge piping, and storage tanks. A schematic diagram of the entire system is shown in Fig. 20.

Liquor is fed to the evaporator by two centrifugal pumps coupled in series to boost the output head. A bypass arrangement, returning part of the liquor being pumped to the feed tank, was available to permit control of the pump discharge pressure. Manual adjustment of a valve on the bypass line was used to obtain the desired head. Normally a high pump discharge head was sought so that a substantial pressure drop was taken over the liquor flow control valve. The liquor flow rate was measured by a magnetic flowmeter and the signal from the magnetic flowmeter was sent to an indicator-controller which in turn controlled the liquor throttling valve. In most of the runs the desired liquor

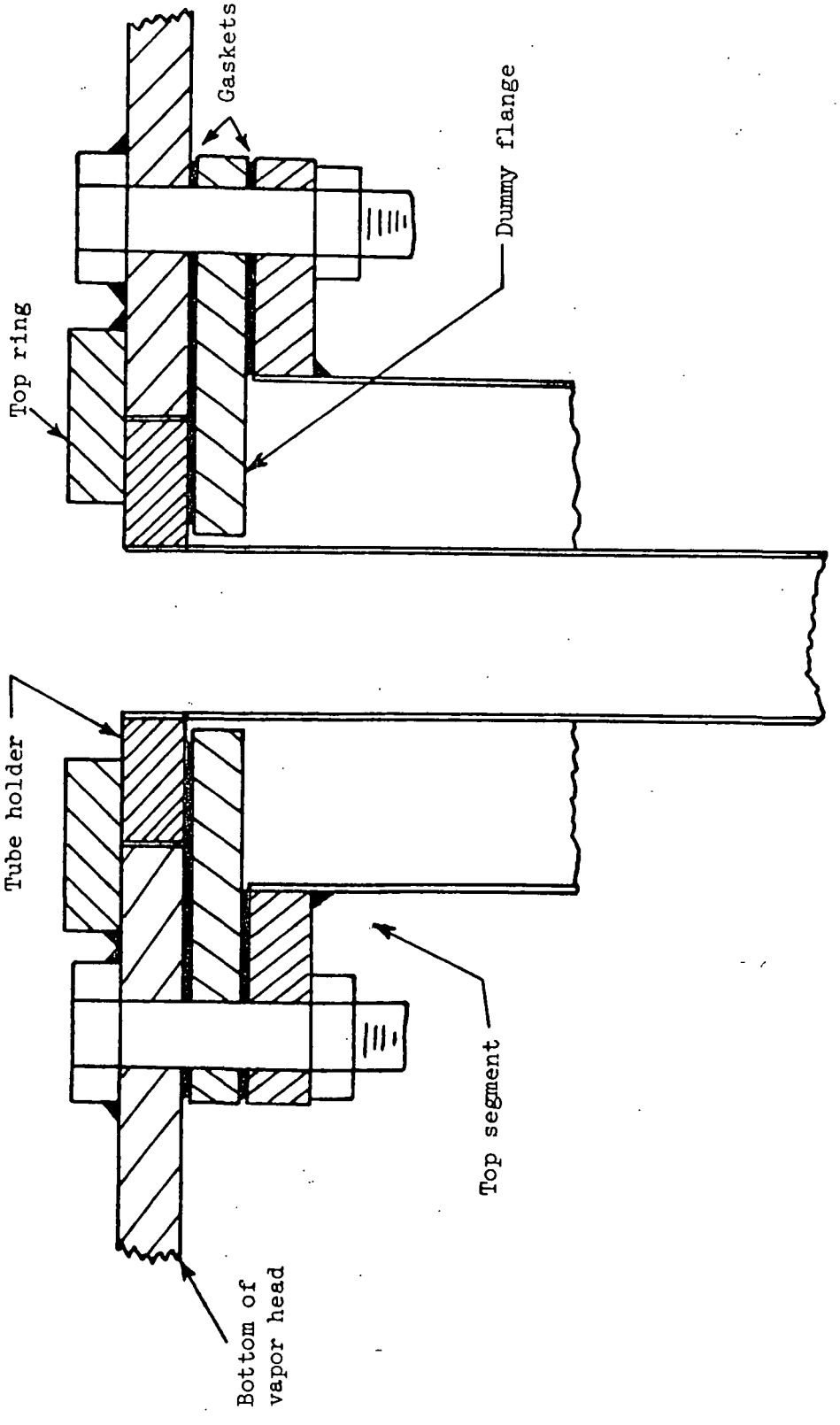

Figure 19. Detail of Method Used to Mount Single-tube Evaporator to Vapor Head

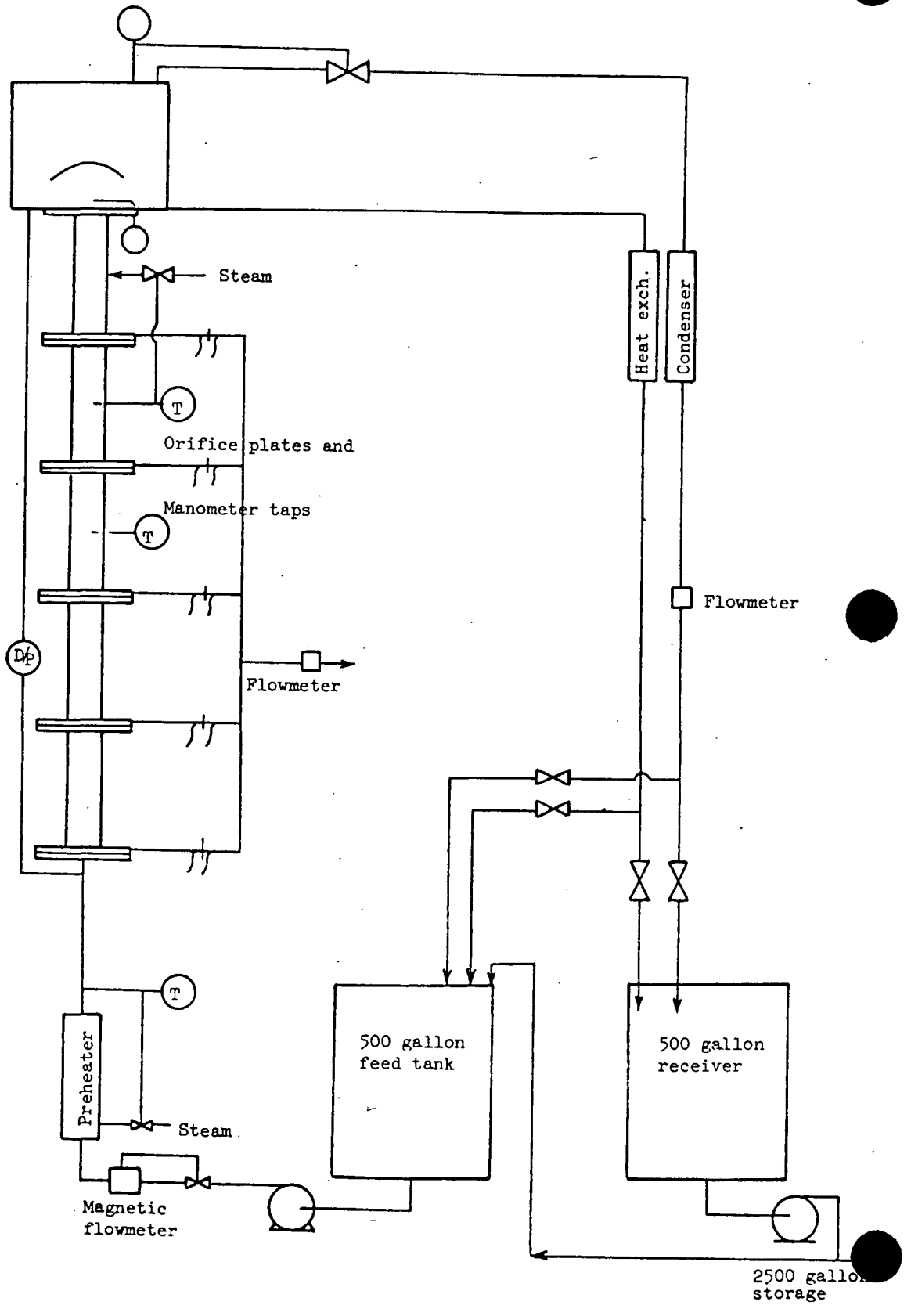

Figure 20. Schematic Diagram of Experimental System

flow rate was near the low end of the range of the magnetic flowmeter. This made it difficult to obtain accurate data on liquor flow rate from the flow recorder. For data purposes, flow rate was determined by direct measurement of the rates of condensate and concentrated liquor returning to the storage tanks.

The inlet temperature to the evaporator was controlled by pumping the feed liquor through a preheater. The preheater is a 4-pass shell and tube heat exchanger with a heat transfer area of 20 ft^2 and a flow cross section of about 0.01 ft^2. The liquor flowed through the tubes. The temperature of the discharge liquor was measured and used to control the steam supply to the preheater. The average residence time of liquor in the preheater was on the order of a minute. This acted as a dead time, and the temperature control system was not always stable. There was some tendency for the feed temperature to oscillate.

The evaporator itself has been described previously. Steam to the evaporator was controlled by a Spence regulator. This was manually adjusted by the operator as needed during the course of the run. The coupling connecting the liquor feed system and the evaporator tube contained taps for temperature and pressure measurements. Temperature was measured with a thermocouple and recorded. A digital display was also available. Pressure was measured with a Pace variable reluctance transducer. It was possible to measure the pressure drop over the tube and the absolute pressure at the feed connection.

The condensed steam which collected within the guarded zones was brought out the bottom flanges and removed through copper tubing. A small orifice meter consisting of a drilled block with two pressure taps was located in the condensate discharge line from each segment. The taps from the five orifice meters were connected to a bank of manometers. The manometer readings gave a measure of the heat transfer rate in each segment.

Downstream of the orifice meters, the individual discharge lines were connected at a small accumulator. The top of the accumulator was connected back to the evaporator shell so that the accumulator was at the same pressure level as the evaporator shell. A sight glass was attached to the accumulator so that the level could be monitored. From the accumulator the total steam condensate passed through an orifice meter (which recorded the flow rate) and a needle valve and then was discharged. The needle valve was adjusted manually as necessary to maintain a fixed level in the accumulator sight glass.

The vapor head is basically a large cylindrical container, 3 feet high and 2 feet in diameter. A domed splash baffle is located about one foot above the evaporator tube discharge to aid separation of liquor and vapor. An internal circular guard ring is attached to the bottom plate about one inch from the edge. This is to keep vapor which condenses on the side of the vapor head from mixing with the concentrated liquor. Ports are present for removal of vapor, concentrator, and condensate from the guard zone. The boiling temperature of the liquor leaving the evaporator tube is measured by a thermocouple located directly above the discharge point. Pressure in the vapor head is controlled by a throttling valve located in the vapor discharge line between the vapor head and the condenser. An indicating pressure controller and pneumatic throttling valve are used to achieve this. In order to improve the stability of this system and to reduce heat losses in the vapor head, air was continuously introduced into the vapor head. This was vented to the atmosphere as a noncondensable gas from the condenser.

The condenser is a shell and tube heat exchanger with about 20 ft^2 of heat transfer area. Vapor flows to the shell side of the unit. Cooling water flows through the tubes. Cooling water flow rate is adjustable. The condensate

is removed from the condenser through a barometric leg. A recording flowmeter is used to monitor the condensate flow rate.

The concentrated liquor flows from the vapor head by gravity and is removed through a barometric leg. The liquor first passes through a heat exchanger to cool it so as to prevent flashing at atmospheric pressure. This cooler is another shell and tube heat exchanger with a heat transfer area of 20 ft^2 and a flow cross section of 0.043 ft^2. Liquor flows through the tube. A manual control valve is located in the discharge piping which can be used as a throttle valve to permit operation at head pressures which exceed the barometric leg capacity.

Two tanks of about 500 gal capacity are located in close proximity to the evaporator loop. The feed tank is a jacketed tank with a stirrer so that the feed liquor can be kept heated and agitated. The other tank is normally used as a receiver. These are connected to two other storage tanks of 2500 gal capacity each. The tanks are interconnected to permit a number of different modes of operation. These are described as follows:

Once-Through, Concentrating: Liquor is periodically pumped from one 2500-gal tank to the feed tank. Concentrated liquor is sent to the receiver tank and the condensate sewered. Periodically, as the receiver fills, the concentrated liquor is pumped over to the second 2500-gal storage tank.

Once-Through, Not Concentrating: Liquor is intermittently pumped from one 2500-gal tank to the feed tank. Both the concentrated liquor and condensate from the evaporator are sent to the receiver tank where they mix.

As the tank fills, the liquor is periodically pumped to the second 2500-gal tank.

Concentrating: A single batch of liquor is supplied to the feed tank. The concentrated liquor from the evaporator is returned to the feed tank while the condensate is sent to the receiver. This causes a gradual increase in the solids content of the liquor in the feed tank.

Full Recirculation: This is also carried out with a fixed amount of liquor. Both the concentrated liquor and condensate are returned to the feed tank and reblended with the feed liquor. This permits continued operation with a nearby constant feed solids content.

Operation can be switched from one mode to the other during a run simply by opening and closing the appropriate valves.

DATA OBTAINED

Although many of the key operating and performance variables were recorded continuously during a run, the data which were analyzed were obtained at discrete intervals. The basic data taken at these intervals are indicated in the sample data sheet shown as Fig. 21.

The pressure at the evaporator bottom and the ΔP over the evaporator were both measured with a Pace variable reluctance transducer. These were measured sequentially by throwing a toggle valve which connects one side of the transducer either to the atmosphere or the vapor head. For each run, it was also necessary to measure how far the pressure transducer was located below the bottom of the evaporator heated section.

Project 3234

REVISED DATA SHEETS

DATE: LIQUOR: RUN NO.:

Time of Day							
Elapsed Time, min							
Bottom Pressure, %							
Δ P, %							
Steam Pressure, psig							
Inlet Temperature, °C							
Vapor Head Temp., °C							
Steam #2, °C							
Steam #3, °C							
Conc. Liquor Flow, g/min							
Condensed Vapor, g/min							
Steam Condensate, g/min							
Manometer #1, cm							
Manometer #2, in							
Manometer #3, cm							
Manometer #4, in							
Manometer #5, cm							
Inlet Solids, % (lab)							
Outlet Solids, % (lab)							
$U_T = \frac{6.9 \times \text{Steam Condensate}}{(T \text{ Steam Ave} - T_{VH})}$							
Inlet Solids, % Cenco							
Outlet Solids, % Cenco							

Figure 21. Sample Data Sheet

The steam pressure was measured with a Bourdon-type gage attached to the shell of the evaporator.

The liquor inlet temperature, the temperature of the boiling liquor leaving the tube (called vapor head temperature on the data sheet), and the steam temperature in the third and fourth segments were all measured with thermocouples. The signal was read from a Westronics model 7201 digital temperature meter which had a resolution of 0.1°C.

The concentrated liquor flow, condensed vapor flow and steam condensate flow (combined for all five segments) were measured by the bucket and stopwatch technique as they were discharged from the system.

Manometer readings which measure the ΔP across the orifice meters in the condensate discharge lines from each of the five segments were recorded. This provides a measure of the heat transfer rate in each segment.

Samples of inlet and discharge liquor were taken each time a set of data was taken. Solids content of these samples were then determined by the revised TAPPI oven-drying procedure (T 650, su-71). A Cenco infrared moisture balance was also used for "on-line" measurement of solids content to serve as an operating guide. An estimate of the overall heat transfer coefficient based on the measured steam condensate flow and the measured temperatures was also made and used as an operating guide.

Thermocouples, orifice meters, and the pressure transducer were calibrated periodically between runs to ensure the validity of the measurements.

APPENDIX II

DATA REDUCTION PROCEDURES

Information on evaporator operating conditions and thermal performance was obtained by measuring certain key variables at discrete time intervals during the run. These key variables and the methods of making the measurements were described in the previous appendix. These data were used as inputs to a computer program which reduced the data to a compatible set of units, checked the accuracy of the data by material and energy balances, calculated temperature and solids profiles along the tube, calculated thermal performance parameters, and outputted the results. A sample of the reduced data output was given in Table V and is reproduced here.

The input data used are summarized as follows:

1. Pressure data:
    a. Pressure at evaporator inlet
    b. Pressure drop across evaporator tube
    c. Steam pressure to evaporator shell
2. Temperature data:
    a. Inlet liquor temperature
    b. Boiling temperature of liquor leaving evaporator tube
    c. Steam temperature in 3rd and 4th segments
3. Flow data:
    a. Flow rate of concentrated liquor discharging from evaporator
    b. Flow rate of condensed vapor discharging from evaporator
    c. Flow rate of total steam condensate

4. Heat distribution data: Manometer readings of orifice meters in condensate discharge lines from each segment
5. Liquor solids content data:
   a. Inlet (or feed) liquor
   b. Concentrated liquor discharging from the evaporator

The data reduction program can be divided into distinct steps. These are described as follows.

1. Data conditioning — unit conversions, correction of pressure data for location of transducers, calculation of total mass flow rate.
2. Calculation of heat transfer rates.
3. Carry out overall balances, compute solids content at evaporator tube discharge by heat balance.
4. Calculate solids content and temperature profiles along the tube.
5. Calculate heat transfer coefficients and their inverses (thermal resistances).
6. Output the data.

DATA CONDITIONING

The total mass flow rate through the evaporator was determined from the measured flow rate of concentrated liquor being discharged and the measured solids content of the feed and discharge liquor. This was considered to be the most accurate estimate of the flow rate available in view of the range problem with the magnetic flowmeter and the loss of water vapor with the air vented from the condenser. The basic relationships used are as follows:

$$W_{in} = W_{CL} \times S_{CL}/S_{in} \tag{19}$$

and

$$W_{vent} = W_{in} - W_{CL} - W_v \tag{20}$$

where

W_{in} = total liquor flow into evaporator, lb/hr

W_{CL} = flow rate of concentrated liquor, lb/hr

S_{CL} = measured solids content of concentrated liquor

S_{in} = measured solids content of inlet liquor

W_{vent} = loss of water vapor out vent, lb/hr

W_v = flow rate of condensed vapor, lb/hr

Heat transfer rates were calculated from the measured manometer readings and the measured combined steam condensate rate. Empirical equations found by calibration were used to convert the manometer readings to flow rate in lb/hr. These values were multiplied by the latent heat of water at shell conditions to get the heat transfer rate in Btu/hr. A subroutine was used to give saturation temperatures, latent heats, and liquid enthalpies as a function of pressure.

Mass and energy balances were used to test the internal consistency of the data. The mass balance was automatically satisfied since the overall mass balance was used to calculate the vent loss. The reasonableness of this value indicates the validity of the flow rate data. A heat balance is used to calculate the solids content of the liquor leaving the evaporator.

$$S_5 = S_{in} \Big/ \left[1 - \frac{Q_T}{W_{in}\lambda} = C_p \frac{(T_{L5} - T_{Lin})}{\lambda} \right] \tag{21}$$

where

S_5 = solids content of liquor leaving Segment 5 (top)

S_{in} = solids content of liquor entering evaporator (bottom)

$\underline{Q_T}$ = heat transfer rate from total steam condensate

λ = heat of vaporization at vapor head pressure

$\underline{C_p}$ = heat capacity of weak liquor

$\underline{T_{L5}}$ = temperature of liquor leaving Segment 5 (top)

$\underline{T_{Lin}}$ = feed liquor temperature

The pressure in the vapor head is found by subtracting the pressure drop over the tube from the pressure at the tube bottom. The heat transfer rates for the individual segments are also added together and compared with $\underline{Q_T}$, the rate determined from the measured total steam condensate discharge rate.

INTERNAL PROFILES

In order to calculate temperature profiles along the evaporator tube it is necessary to consider two distinct regions in the evaporator, the subcooled zone and the net boiling zone. In the subcooled zone only sensible heat is supplied and the liquor temperature rises as heat is transferred in. The subcooled zone persists until the liquor temperature is raised to the boiling temperature. From this point on, net boiling exists. In the net boiling zone, the liquor is at the boiling temperature. This will vary along the tube because of two effects:

1. The changing pressure along the tube.
2. The change in the boiling point rise to the liquor because of the changing solids content along the tube.

Thus, in order to calculate the temperature profile it is necessary to construct the pressure profile and solids profile. This must be done from measured values at the top and bottom of the evaporator and the heat transfer distribution.

PRESSURE PROFILE

The pressure profile is calculated in the following manner. In the subcooled region the pressure changes only because of the gravity head. Thus,

$$P = P_{in} - \rho_L \, g \, Z \tag{22}$$

where

P = pressure at position Z in subcooled zone

P_{in} = pressure at evaporator bottom

ρ_L = liquor density

g = gravitational acceleration

Z = position coordinate increasing in the upward direction with origin at the tube bottom

The pressure at the point of the inception of net boiling is given by:

$$P_* = P_{in} - \rho_L \, g \, L_* \tag{23}$$

where

L_* = length of the subcooled zone

In the net boiling region the pressure change is more complex and not readily predictable. In this analysis, it is assumed that the pressure changes in a linear manner from the value at the end of the subcooled zone to the value at the tube discharge.

$$\therefore \quad P = P_* - \frac{(P_* - P_5)}{(L_T - L_*)} (Z - L_*) \quad \text{for} \quad Z > L_* \tag{24}$$

where

P_5 = pressure at end of Segment 5 = $P_{in} - \Delta P$

L_T = total heated length = 19 feet

SOLIDS PROFILE

The solids profile was calculated in the following manner. In the subcooled region the solids content remains constant at the inlet value. In the net boiling zone the solids content is dependent on the heat balance. The contribution of flashing *per se* was neglected when computing the solids profile, since the flash vapor is small compared to that generated by heat transfer in the net boiling zone and its explicit inclusion leads to a nonlinear coupling of the solids with the temperature distribution (since the amount of flashing depends on dT_L/dZ). The solids profile is calculated based on the assumption that the vapor flow at any point in the net boiling region is proportional to the amount of heat transferred between that point and the start of the net boiling zone. The total heat transfer rate in the net boiling zone is given by:

$$Q_v = \sum_{j=1}^{5} Q_j - W_{in} C_p (T_* - T_{in}) \qquad (25)$$

where

Q_v = total heat transfer rate in net boiling zone

Q_j = heat transfer rate in jth segment

T_* = liquor temperature at start of net boiling zone

Thus, it is assumed that

$$\frac{W_v(Z)}{W_{v5}} = \frac{\int_{L_*}^{Z} (Q_j/L_s)dZ}{Q_v} \qquad (26)$$

where

$W_v(Z)$ = vapor flow rate at position Z

W_{v5} = vapor flow out of Segment 5

L_s = length of an individual segment = 3.8 feet

$$W_{v5} = W_{in} \frac{(S_5 - S_{in})}{S_5} \tag{27}$$

The solids content at any position is related to the vapor flow at that position by:

$$S(Z) = \frac{S_{in} W_{in}}{[W_{in} - W_v(Z)]} \tag{28}$$

TEMPERATURE PROFILES

The temperature profile is calculated from the heat balance in the subcooled zone and from the pressure and solids profile in the net boiling zone. The heat flux is assumed to be uniform within a given segment. Thus, in Segment 1 the liquor temperature is given by:

$$T_L = T_{Lin} + \frac{Q_1}{W_{in} C_p} \frac{Z}{L_s} \quad \text{for } Z < L_* \tag{29}$$

If $L_* > L_s$, then the subcooled zone extends beyond the first segment. In this case, Equation (29) holds for the first segment and

$$T_L = T_{L1} + \frac{Q_2}{W_{in} C_p} \frac{Z}{L_s} \quad \text{for } Z < L_* \tag{30}$$

where

$$T_{L1} = T_{Lin} + \frac{Q_1}{W_{in} C_p} \tag{31}$$

This procedure continues until $Z \geq L_*$. In the net boiling zone the temperature is given by

$$T_L = T_{sw}(P) + \theta(S) \tag{32}$$

where

T_{sw} = saturation temperature of water at pressure P

θ = boiling point rise of the liquor at solids content S

The saturation temperature of water is obtained from a properties subroutine. The boiling point rise is based on the assumption that the b.p. rise is related to the solids content by an equation of the form

$$\theta = K\left(\frac{S}{1 - S}\right) \tag{33}$$

The constant K is evaluated from the measured temperature, pressure, and solids content of the liquor at the tube discharge.

$$K = T_{L5} - T_{sw}(P_5)\ \frac{(1 - S_5)}{S_5} \tag{34}$$

SUBCOOLED LENGTH

The calculation of the subcooled length (L_*) is based on finding the value of Z at which the temperature vs. position lines for the actual liquor temperature and the boiling temperature intersect. The saturation temperature of water as a function of pressure was fitted to an empirical equation:

$$T_{sw} = 100 + 1.86P - 0.0342P^2 \quad (\text{in } ^\circ C) \tag{35}$$

The value of L_* was then found by solving the equation:

$$T_{Lin} + \frac{Q_1}{W_{in} C_p}\frac{L_*}{L_s} = \theta_{in} + 100 + 1.86(P_{in} - \delta_L g L_*) - 0.0342(P_{in} - \delta_L g L_*)^2 \tag{36}$$

where

$$\theta_{in} = K\ \frac{S_{in}}{(1 - S_{in})} \tag{37}$$

If $L_* > L_s$, the equation for the subcooled liquor temperature in the second segment would have to be used, etc.

HEAT TRANSFER COEFFICIENTS

Heat transfer coefficients are calculated as follows. An overall heat transfer coefficient for the entire evaporator is calculated from the total heat transfer rate based on the combined steam condensate and the difference between the steam temperature and the liquor temperature at the tube discharge.

$$U_o = \frac{Q_T}{A_T(T_s - T_{L5})} \tag{38}$$

where

A_T = total heat transfer area = 9.95 ft^2

T_s = steam temperature

The value of the steam temperature used in calculating heat transfer coefficients was the average of the thermocouple readings in the third and fourth segments.

Segment heat transfer coefficients were calculated from the measured heat transfer rates in the segments and the average liquor temperature in that segment.

$$U_i = \frac{Q_i}{A_s(T_s - \overline{T}_{Li})} \tag{39}$$

A_s = segment heat transfer area = 1.99 ft^2

$$\overline{T}_{Li} = \frac{1}{L_s} \int_{Z = (i-1)L_s}^{Z = iL_s} T_L(Z)dZ \tag{40}$$

OUTPUT

Most of the output variables in Table IV are self-explanatory. The first grouping specifies evaporator operating variables. The next, the overall heat transfer rate and the overall coefficient and its inverse. This is followed by the exit solids as found by heat balance and the measured discharge

solids. Next is temperature data. TSA is the average of the steam temperatures in the third and fourth segments. TS is the saturation temperature corresponding to the measured steam pressure. TVH is liquor temperature entering the vapor head. DELTA T is the thermal driving force = TSA-TVH. The inlet subcooling is the difference between TVH = T_{L5} and the inlet liquor temperature T_{Lin}. The next line gives information on the location of conditions at the end of the subcooled zone.

Positions are coded as follows. Position 0 is the inlet to the evaporator. Position i is at the end of the ith segment. Data on pressure, solids content, liquor temperature, local boiling temperature and boiling point rise are included.

Data on segment heat transfer rates, coefficients and inverse coefficients are given next. U_B is a heat transfer coefficient using an average boiling temperature in that segment in calculating the driving force. It differs from the normal segment coefficient only in the nonboiling zone.

The final lines are data consistency checks. The sum of the segment heat transfer rates are compared with the total. In addition, the breakdown of discharge flows between concentrated liquor (WLOUT), condensed vapor (WVOUT) and the vent loss is also given.